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Handbook on In situ Treatment of Hazardous Waste-Contaminated Soils

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16. ABSTRACT

This handbook is intended to assemble state-of-the-art information on in situ treatment technologies for hazardous waste - contaminated soils. Extensive references are provided for those who wish to seek more detail on a given topic. The Risk Reduction Engineering Laboratory is continuing with its research on in situ treatment to improve on technologies discussed in this handbook and to explore new technologies.

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Risk Reduction Engineering Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

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Executive Summary

Purpose and Scope

This handbook comprises an update of Volume 1 of the 1984 USEPA document entitled "Review of In-Place Treatment Techniques for Contaminated Surface Soils." The purpose of this handbook is the same as that of the original document - to provide state-of-the-art information on in situ treatment technologies for contaminated soils. Like the previous document, this handbook is written for the use of a varied audience with diverse technical backgrounds.

The information presented herein is detailed enough to provide the reader with adequate data for an initial evaluation of the applicability of a technology in certain situations, yet general enough to be useful and informative to those whose backgrounds are not highly technical. Extensive references are provided for the reader's use in obtaining additional details on these technologies.

An in situ treatment technology is defined as one that can be applied to treat the hazardous constituents of a waste or contaminated environmental medium where they are located and is capable of reducing the risk posed by these contaminants to an acceptable level or completely eliminating that risk. In situ treatment implies that the waste materials are treated without being physically removed from the ground.

The handbook is divided into four sections. Section 1 provides an introduction and background for the handbook. Section 2 provides a general overview of the legislation and regulations pertaining to Superfund site remedial activities that have been instrumental in promoting the development of in situ treatment technologies. Section 3 presents state-of-the-art information on in situ treatment technologies. It includes a description of each technology process; the wastes amenable to treatment; the ease of application; potential level of treatment available; reliability of the method; current status of the technology; secondary impacts; equipment, exogenous reagents, and information required; and sources of information. Section 4 addresses delivery and recovery technologies. A brief discussion of techniques for the modification of soil properties is presented in the appendix.

The 1984 document consisted of two volumes. Only Volume 1 is being updated by this handbook. The reader can refer to Volume 2, however, for a still current and comprehensive discussion of the fundamental properties of soil/waste systems.

Legislative and Regulatory Overview

Methods for cleaning up hazardous waste sites have changed since 1980 when the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), or Superfund, was enacted. Early remedial actions for contaminated soils consisted primarily of excavation and removal of the contaminated soil from the site and disposal at a landfill. Congress has recently enacted legislation that prohibits the land disposal of hazardous wastes unless the USEPA determines otherwise [i.e., Hazardous and Solid Waste Amendments (HSWA)] and encourages permanent treatment of contaminated substances [i.e., Superfund Amendments and Reauthorization Act (SARA)]. In many cases, in situ treatment of contaminated soils and hazardous waste can effect permanent and significant reductions in the volume, toxicity, and mobility of hazardous substances.

Remediation of hazardous waste sites requires striking a balance between the desire to characterize site risks quickly and to analyze alternative remedial approaches to begin the cleanup while still meeting all the CERCLA mandates. In the proposed revision of the National Contingency Plan (NCP)

EPA fulfills both of these requirements through an approach that examines the characteristics of sites and evaluates alternative methods for remediation in a streamlined remedial action process.

Treatment alternatives are subjected to detailed analysis consisting of a complete assessment of each alternative as it relates to nine criteria encompassing the recommendations and mandated requirements of CERCLA as amended by SARA. These criteria are as follows:

1) Overall protection of human health and the environment
2) Compliance with applicable or relevant and appropriate requirements (ARARs)
3) Long-term effectiveness and permanence
4) Reduction of toxicity, mobility, or volume
5) Short-term effectiveness
6) Implementability
7) Cost
8) State acceptance
9) Community acceptance

In Situ Treatment Technologies

Detailed information on specific in situ treatment technologies in the following categories is provided:

- Soil flushing
- Solidification/stabilization
- Degradation
- Control of volatile materials
- Chemical and physical separation techniques

Table ES-1 summarizes the in situ treatment technologies discussed in the handbook in relation to the waste amenable to treatment and the status of the technology development.

Soil Flushing

Soil flushing is the washing of contaminants from the soil with a suitable solvent such as water or other aqueous or nonaqueous solutions. The method is potentially applicable to all types of soil contaminants. Several bench- and pilot-scale studies have been completed on the effectiveness of soil flushing. Soil flushing in conjunction with bioremediation may be a cost-effective means of soil remediation at certain sites. Soil flushing enables permanent removal of contaminants from the soil and is most effective in permeable soils. The technology can introduce potential toxins into the soil system. An effective collection system is required to prevent contaminant migration.

Solidification and Stabilization

Solidification and stabilization refer to treatment processes that are designed to accomplish one or more of the following:

- Improve handling and physical characteristics of the waste by producing a solid from liquid or semiliquid wastes.
- Reduce contaminant solubility in the treated waste.
- Decrease the exposed surface area across which transfer or loss of contaminants may occur.

Table ES-1. Summary Matrix of Treatment Technologies

Technology	Wastes amenable to treatment	Status
Soil Flushing	Soluble organics and inorganics	Pilot scale
Solidification/stabilization		
Pozzolan-portland cement	Inorganics	Pilot scale
Lime-fly ash pozzolan	Inorganics	Pilot scale
Thermoplastic microencapsulation	Inorganics, organics	Laboratory
Sorption	Inorganics	Pilot scale
Vitrification	Metals, inorganics, organics	Pilot scale
Degradation		
Oxidation		
Soil catalyzed reactions	Aliphatic organics, other organics	Limited field
Oxidizing agents	Various organics	Field scale
Reduction		
Organics	Chlorinated organics, unsaturated aromatics, aliphatics	Field scale
Chromium	Hexavalent chromium	Limited field
Selenium	Hexavalent selenium	Limited field
Dechlorination	PCB, dioxin, halogenated compounds	Limited field
Polymerization	Aliphatics, aromatics, oxygenated organic compounds	Limited field
Biodegradation		
Colloidal gas aphrons	Organics	Bench and pilot
Soil moisture	Organics	Field scale
Soil oxygen - aerobic	Organics	Field scale
Soil oxygen - anaerobic	Halogenated organics	Conceptual
Soil pH	Organics	Field scale
Nutrients	Organics	Field scale
Temperature	Organics	Field scale
Nonspecific organic amendments	Organics, arsenite wastes	Laboratory
Cometabolism		
Analogue enrichment	Some organics with analogues	Laboratory
Nonanalogue enrichment with methane	Chlorinated solvents	Laboratory
Other nonanalogue hydrocarbon substrates	Organics	Laboratory
Exogenous acclimated or mutant microorganisms	Various organics	Field scale
Cell-free enzymes	Organics	Laboratory
Photolysis		
Proton donors	Some organics, including TCDD, kepone, PCB	Field scale
Enhanced volatilization	Specific organics	Laboratory
Control of volatile materials		
Soil vapor extraction	Volatile, semivolatile organics	Field scale
Radio frequency heating	Solvents and fuels	Pilot scale
Soil cooling	Volatile organics	Bench scale
Chemical and physical separation		
Permeable barriers	Organics and inorganics	Bench, pilot scale
Electrokinetics	Ionic metal species	Pilot scale
Ground freezing	Volatile organics	Bench scale

Solidification techniques eliminate the free liquid, increase the bearing strength, decrease the surface area of the waste material, and produce a monolithic solid product of high structural integrity. Solidification may involve encapsulation of fine waste particles (microencapsulation) or large blocks of wastes (macroencapsulation). Chemical interactions do not necessarily occur between the wastes and the solidifying agents, but the waste material is mechanically bound within the solidified matrix in such a way that hazardous substances cannot be released upon exposure to air, water, soil, or mild acidic conditions.

Stabilization refers to the process of reducing the hazardous potential of waste material by converting the contaminants into their least soluble, mobile, or toxic form. This technique does not necessarily change the physical characteristics of the waste.

Solidification/stabilization techniques have been widely used in low-level radioactive waste disposal. Their application to hazardous wastes is becoming more common, however, and many vendors are studying and developing processes that are directly applicable to hazardous waste-contaminated soils and sludges.

Waste solidification/stabilization systems that are potentially useful in remedial action activities are as follows:

- Pozzolan-portland cement systems
- Lime-fly ash pozzolan systems
- Thermoplastic microencapsulation
- Sorption
- Organic binding

In situ vitrification is a thermal treatment process by which contaminated soils are converted into chemically inert and stable glass and crystalline materials. Large electrodes are inserted into contaminated soils, and heat (up to 3600°C) is generated by passing electric current through the electrodes. In situ vitrification has been used to stabilize low-level radioactive wastes.

Degradation

Chemical degradation, biodegradation, and photolysis may be effective in situ treatment technologies.

Chemical Degradation

Oxidation, reduction, dechlorination, and polymerization reactions may be carried out in situ to transform soil contaminants into less toxic or less mobile products.

Chemical oxidation increases the oxidation state of an atom by removing electrons or adding oxygen to the atom. Oxidation may cause a substance to be transformed, degraded, or immobilized in soil. Oxidation reactions within the soil matrix may occur through management of the natural processes in a soil or through addition of an oxidizing agent to the soil-waste complex.

Chemical reduction is a process in which the oxidation state of an atom is decreased. Reducing agents are electron donors, and reduction is accomplished by the addition of electrons to the atom. Reduction of chemicals may occur naturally within the soil system. Certain compounds are more susceptible to reduction than others because they will accept electrons. The addition of reducing agents to soil to degrade reducible compounds can be used as an in situ treatment technology.

Chemical dechlorination processes use specially synthesized chemical reagents to destroy hazardous chlorinated molecules or to detoxify them to form other compounds that are considered less harmful. In recent years, several dechlorination processes using different reagents have been developed to detoxify PCBs and many chlorinated organic compounds. These processes were first developed for the treatment of PCB-containing oils, but several have potential application to in situ treatment of contaminated soils.

A polymerization reaction is the conversion of a particular compound to a larger chemical multiple of itself. The resulting polymer often has physical and chemical properties different from the initial unit, and it could be less mobile in the soil system. Chemical polymerization is most effective for immobilization of organic constituents, preferably those with more than one double bond. General categories of constituents suitable for polymerization include aliphatic, aromatic, and oxygenated monomers such as styrene, vinyl chloride, isoprene, and acrylonitrile.

Biodegradation

Biodegradation refers to the breakdown of organic compounds in soils by the action of microorganisms such as bacteria, actinomycetes, and fungi. Treatment generally consists of optimizing conditions of pH, temperature, soil moisture content, soil oxygen content, and nutrient concentration to stimulate the growth of microorganisms that will feed on the particular contaminants present. Alternatively, genetically engineered organisms may be added to the soil system and conditions established within the soil to optimize their growth. Some of the hazardous constituents present in a contaminated soil may be most readily biodegraded under aerobic conditions, whereas others are more readily degraded under anaerobic conditions. Treatment might, therefore, consist of alternate aerobic and anaerobic cycles.

Photolysis

Photochemical reactions require the absorption of light energy, generally from sunlight in natural systems. Because light does not penetrate very far into soils, photodegradation of soil contaminants is limited to soil surfaces. The addition of proton donors in the form of polar solvents such as methanol can enhance surface photodegradation of soil contaminants.

Control of Volatile Materials

Concentrations of volatile materials can be reduced by the use of various vapor extraction systems. Vapor extraction systems involve the recovery of volatile contaminants by injecting air or steam into the soils and extracting the air (in which volatile chemicals have partitioned) in a vapor-recovery well.

Radio frequency (RF) heating is a technique for rapid and uniform in situ heating of large volumes of soil. It can be used to volatilize materials such as chlorinated solvents and the aliphatic and aromatic fractions of jet fuels and gasoline. The volatilized materials are then collected and treated.

Soil cooling may be used to decrease soil temperatures as a means of reducing the vapor pressure of volatile constituents and thus their volatilization rates. Cooling agents are applied, such as dry ice or liquid nitrogen. This technology is currently in the bench-scale stage of development.

Chemical and Physical Separation Techniques

Chemical contaminants can be removed from soil particles by physical and chemical means. This subsection discusses three such techniques: 1) permeable barriers, 2) electrokinetics, and 3) ground freezing. (Although permeable barriers are not directly used for soil treatment, the technology is an important in situ method for treating hazardous waste landfill leachate and is thus presented here.)

Migration of leachate from hazardous waste deposits (i.e., landfills) presents a significant obstacle in attempts to remediate hazardous waste sites. Permeable barriers, which may be used to retain contamination within site boundaries, represent a potentially effective method of in situ treatment. The technology incorporates the use of readily available materials to adsorb contaminants from ground water as the contaminated plume migrates through the permeable barrier unit.

Electrokinetics has been used for more than 50 years to dewater and stabilize soils. It is hoped that it will produce similar results at hazardous waste sites. An electrokinetic phenomenon referred to as electroosmosis occurs when a liquid migrates through a charged porous medium under the influence of a charged electrical field. The charged medium is usually some kind of clay, sand, or other mineral particles that characteristically carry a negative surface charge. When the charged particles come into contact with water molecules, they attract positive ions, which effectively neutralize their negative surface charge. As a result, cations predominate in the layer of water next to the surfaces of the particles and create what is referred to as a "diffuse double layer."

If an electric field is applied to the saturated medium through anodes, cations bound in the diffuse double layer will migrate toward the negatively charged cathode. The viscous drag of water molecules due to the migration of the cations produces a net flow of water toward the cathode. The application of an electrical field induces the water to flow.

Artificial ground freezing has been shown in laboratory studies to be a potentially effective method of driving volatile organic contaminants from soil matrices. Artificial ground freezing was used to facilitate decontamination of soils and the dewatering of slurries in the bench-scale demonstration. Contaminants are removed from soils by utilizing the differences in physical and chemical properties of the water and contaminants within the soil.

Delivery and Recovery Systems

Delivery and recovery technologies refer to methods that facilitate the transport of materials either into or out of the subsurface. Delivery and recovery techniques are integral to some of the in situ treatment technologies such as biodegradation, vapor extraction, and solidification/stabilization. Delivery and recovery technologies have been developed largely by the petroleum and mining industries. Research is currently under way to adapt some of these techniques to the treatment of hazardous wastes.

Time Frame

This report covers a period from May 1988 to July 1989, and work was completed as of November 1989.

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Section 1
Introduction

1.1 Purpose

This handbook comprises an update of Volume 1 of the 1984 document entitled "Review of In-Place Treatment Techniques for Contaminated Surface Soils" (Sims and Bass 1984). The purpose of the original document was to provide state-of-the-art information on in situ treatment technologies for contaminated soil. Like the previous document, this handbook is written for the use of a varied audience with diverse technical backgrounds, such as On-Scene Coordinators (OSCs), Remedial Project Managers (RPMs), State and local regulatory personnel, and others involved in the selection of remedial actions for soils contaminated by hazardous substances.

The information presented herein is detailed enough to provide the reader with adequate data for an initial evaluation of the applicability of a technology in certain situations, yet general enough to be useful and informative to those whose backgrounds are not highly technical. Extensive references are provided, and the reader is encouraged to seek additional details from these sources.

For purposes of this handbook, an in situ treatment technology is defined as one that can be applied to treat the hazardous constituents of a contaminated environmental medium where they are located and is capable of reducing the risk posed by these contaminants to an acceptable level or completely eliminating that risk. In situ treatment implies that the waste materials (i.e., contaminated soils) are treated without being physically removed from the ground. In situ removal, that is removing contaminants without removing the soils, is also discussed in this handbook.

The technologies presented in this handbook have been demonstrated at various levels ranging from bench or laboratory scale to field implementation. Although some of the technologies addressed have not been tested in situ, they are presented here because their in situ application may be feasible in the future.

1.2 Background

Legislation, recently promulgated regulations, and the high costs associated with treating large volumes of contaminated soils have prompted the development of technologies for the in situ treatment of contaminated soils and other hazardous wastes. The original report (Sims and Bass 1984) described large numbers of chemical and physical processes (e.g., oxidation, reduction, precipitation, ion exchange) that have potential for in situ application to immobilize or detoxify contaminants in the soil. Many of these technologies were conceptual in nature or had been tested only at the bench scale. Most of the technologies involve aqueous solution chemistry, and it was hoped that workable in situ treatment would be developed along these lines. Instead, major developments have involved biodegradation, solidification/stabilization, and removal of contaminants.

Another area of significant research concerns delivery and recovery technologies, i.e., processes that facilitate the transport of materials either into or out of the subsurface. Murdoch et al. (1988) define delivery technologies as involving "the transport of materials into the subsurface. Liquids are the principal phase used in most delivery operations, although some of the new techniques will allow either vapor or solid phases to be delivered as well." Similarly, recovery technologies are described as including "any process used to remove materials from the subsurface. The principal recovery technologies used for remediation are associated with fluid flows driven by hydraulic gradients." Also used are "... technologies driven by other types of processes, such as thermal methods, as well as processes that expedite recovery by chemical reactions that alter the behavior of contaminants."

Delivery and recovery techniques are integral to some of the in situ treatment technologies, such as bioremediation, vapor extraction, and solidification/stabilization. Delivery and recovery technologies have been developed largely by the petroleum and mining industries. Research is currently under way to adapt some of the delivery/recovery techniques to the treatment of hazardous wastes. The preliminary research is discussed in this document.

1.3 Special Considerations for In Situ Treatment

The mechanism of in situ treatment may be physical, chemical, thermal, biological, or a combination of these. The location of treatment (i.e., in situ), however, imposes unique constraints on the application and effectiveness of the treatment process. Thorough site characterization is critical to the proper evaluation of the feasibility of applying any in situ treatment technology. The site characterization (i.e., physical, chemical, and biological characteristics) should be tailored to the specific technology under consideration. Bench- and pilot-scale treatability studies should be designed and conducted with site characteristics in mind. There are several guidance documents available concerning site characterization and treatability testing (USEPA 1985; Amdurer et al. 1986; USEPA 1988) that should be referred to during the remedial action process to ensure a rational approach to the selection, design, and implementation of specific in situ treatment technologies.

Monitoring the effectiveness of the in situ treatment process also requires special consideration and planning and could have a major impact on the overall cost of implementing an in situ treatment technology. Subsurface geologic and hydrologic conditions may cause treatment agents to be diverted away from target areas and thus limit treatment effectiveness. Numerous samples may need to be collected and analyzed to verify the uniformity and successfulness of treatment. A carefully developed sampling strategy will be necessary as part of the technology implementation.

1.4 Overview of the Handbook

The handbook is divided into four sections. Section 2 provides a general overview of the legislation and regulations pertaining to Superfund site remedial activities that have been instrumental in promoting the development of in situ treatment technologies. Section 3 presents state-of-the-art information on in situ treatment technologies. It includes a description of each technology or process; the wastes amenable to treatment; the ease of application; potential level of treatment available; reliability of the method; current status of the technology; secondary impacts; equipment, exogenous reagents, and information required; and sources of information. Section 4 addresses delivery and recovery technologies. A brief discussion of techniques for the modification of soil properties is presented in the appendix.

The 1984 document consisted of two volumes. Only Volume 1 is being updated by this handbook. The reader can refer to Volume 2 (Sims 1984), however, for a still current and comprehensive discussion of the fundamental properties of soil/waste systems. The discussion includes physical soil properties, soil sorption, soil microbiology, and volatilization and degradation as related to hazardous waste treatment in soil systems.

Section 2
Legislative and Regulatory Overview

Methods for cleaning up hazardous waste sites have changed since 1980 when the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), or Superfund, was enacted. Early remedial actions for contaminated soils consisted primarily of excavation and removal of the contaminated soil from the site and disposal at a landfill. This, in effect, moved the problem from one location to another. Subsequent findings of leaking landfills and heightened public concern about the problem have resulted in a shift in public policy concerning cleanup of hazardous waste sites. Specifically, Congress has enacted legislation that prohibits the land disposal of hazardous wastes unless EPA determines otherwise [i.e., Hazardous and Solid Waste Amendments (HSWA)] and encourages permanent treatment of contaminated substances [i.e., Superfund Amendments and Reauthorization Act (SARA)].

In many cases, in situ treatment of contaminated soils and hazardous waste can effect permanent and significant reductions in the volume, toxicity, and mobility of hazardous substances. The U.S. Environmental Protection Agency (EPA) Office of Research and Development, through several research studies such as the Superfund Innovative Technology Evaluation (SITE) Program and the SARA Best Demonstrated Available Technology (BDAT) Program, is investigating promising treatment technologies for contaminated Superfund site soils. In situ treatment technologies are also being developed and tested in Europe and Japan. A NATO/CCMS program has been instituted to study technologies for the treatment of contaminated ground water and soils.

The following sections present a general overview of the legislation and regulations that have influenced the development of some of the in situ treatment technologies for the treatment of hazardous waste.

2.1 Comprehensive Environmental Response, Compensation, and Liability Act

In 1980, Congress enacted CERCLA, the first comprehensive Federal law addressing releases of hazardous substances into the environment. The primary goal of CERCLA (or Superfund), was to establish an organized cost-effective mechanism for responding to releases of hazardous substances or to abandoned or uncontrolled hazardous waste sites that posed a serious threat to human health and the environment. To accomplish this goal, CERCLA mandated two types of response capabilities: 1) an emergency response action for handling major chemical spills or incidents requiring immediate action, and 2) a remedial response capability for undertaking the long-term cleanup of abandoned hazardous waste disposal sites. The regulatory framework developed to guide these responses became the new National Contingency Plan (NCP). Revised in 1982 and again in 1985, the NCP first outlined the level of cleanup necessary at a Superfund site and established basic procedures to be followed for discovery or notification, response, and remediation of a hazardous waste site (Hall and Bryson 1985).

2.2 Superfund Amendments and Reauthorization Act

The Superfund Amendments and Reauthorization Act of l986 (SARA) added several important, new dimensions to CERCLA, such as increased emphasis on health assessments and consideration of air releases. One of the most far-reaching provisions, however, Section 121, Cleanup Standards, which stipulates rules for the selection of remedial actions, provides for a review of those actions, describes requirements for the degree of cleanup, and mandates conformance with the National Contingency Plan whenever practicable. It strongly recommends that remedial actions use onsite treatment that "... permanently and significantly reduces the volume, toxicity, or mobility of hazardous substances ..." and requires selection of a remedial action that is "... protective of human health and the environment, that is cost-effective, and that utilizes permanent solutions and alternative treatment technologies or resource recovery technologies to the maximum extent practicable" (PL 99-499).

Another SARA requirement is that remedial actions meet all applicable or relevant and appropriate (ARAR) Federal standards and any more stringent State standards. "Applicable requirements" refer to those standards, requirements, criteria, or limitations that specifically address a hazardous substance, pollutant, contaminant, remedial action, location, or other circumstance at a CERCLA site. "Relevant and appropriate requirements" refer to those cleanup standards that, although not applicable, address problems or situations sufficiently similar to those encountered at the site so that their use is suitable.

As amended by SARA, CERCLA sets rigorous remedial-action cleanup standards. It emphasizes achieving protection that will endure by mandating the use of permanent solutions, and it expresses a clear preference for achieving this protection through the use of treatment technologies as the principal element of remediation. Clearly, the most permanent solution is attained by remedies that do not rely heavily on long-term operation and maintenance; however, because of the variety of releases and threats encountered at hazardous waste sites, specific remedial actions and cleanup levels must be determined on a site-by-site basis. The function of the National Contingency Plan is to delineate how such site-specific decisions will be made.

2.3 National Contingency Plan

Remediation of hazardous waste sites requires striking a balance between the desire to characterize site risks quickly and to analyze alternative remedial approaches to begin the cleanup while still meeting all the CERCLA mandates. In the proposed revision of the National Contingency Plan (USEPA 1988), EPA fulfills both of these requirements through an approach that examines the characteristics of sites and evaluates alternative methods for remediation in a streamlined remedial action process. The five steps involved in this process are as follows:

1) Project scoping
2) Remedial investigation
3) Feasibility study
4) Selection of an action
5) Documentation

The first step, project scoping, is the development and planning phase of the project. It involves defining the appropriate type and extent of investigative and analytical studies that should be undertaken. During this phase, the remedial investigation and feasibility studies are planned and a preliminary site characterization is developed. Both the quality and the quantity of data necessary for a full site evaluation should be determined, and studies that will result in these data should be selected. Potential ARARs are identified, and preliminary remediation objectives for the protection of human health and the environment are formulated.

The purpose of a remedial investigation, the second step, is to gather sufficient data to characterize the site conditions and to assist in the selection of an appropriate response action. Of particular interest are any data that will affect the type and extent of possible treatment or recycling approaches. Preliminary treatability studies should be performed to make a better evaluation of potential technologies. A site-specific baseline risk assessment consisting of an exposure assessment and a toxicity assessment is also initiated during the remedial investigation. Chemical-specific toxicity information is analyzed along with critical assumptions and uncertainties so that all significant risks can be identified.

The third step, the feasibility study, is the real heart of the remedial action process. During this phase, viable remedial alternatives are analyzed based on nine criteria related to CERCLA's mandates. In the selection of these alternatives, the lead agency must first refine the remedial action objectives developed during the planning stage. Contaminants and media of concern, potential exposure pathways, and remediation goals should be specified. Risks associated with potential alternatives are assessed based on a reasonable maximum exposure scenario that will insure that exposure levels are both protective and attainable. Once these objectives have been established, potential technologies are identified, briefly evaluated to verify their suitability, and assembled into remedial alternatives.

The range of alternatives selected for detailed analysis should represent distinct, promising approaches to managing site problems. In view of the statutory preference for treatment remedies, this range should include alternatives that feature treatments that will reduce the toxicity, mobility, or volume of the hazardous substance at the site. Included in CERCLA is the flexibility to examine and select technologies not yet proven in practice to promote the development of new methods of hazardous waste treatment. Thus, innovative technologies may also be selected for detailed analysis if these technologies are believed to offer significant advantages over other options being considered.

The number and type of remedial alternatives should be tailored to fit the site and the remedial action objectives. The variety of options considered should not be limited simply because of quantity. Should a preliminary screening become necessary to reduce the number of alternatives analyzed in detail, however, the primary factors for consideration are effectiveness, ease of implementation, and cost. Effectiveness refers to the overall potential of a technology to eliminate, reduce, or control current and potential risks; ease of implementation includes technical, administrative, and logistical problems. Cost should be considered in conjunction with other factors to determine whether an option is likely to yield cost-effective results.

Viable treatment alternatives that have fulfilled the aforementioned requirements are subjected to a detailed analysis, i.e., a complete assessment of each alternative as it relates to nine criteria encompassing the recommendations and mandated requirements of CERCLA as amended by SARA. These criteria are as follows:

1) *Overall protection of human health and the environment.* Mandated by CERCLA, this is the primary goal of any remediation program. A selected remedy must adequately eliminate, reduce, or control all current and potential risks.

2) *Compliance with applicable or relevant and appropriate requirements (ARARs).* Also as mandated by CERCLA, Federal and State agencies must cooperate to identify ARARs early in the remediation process. Remedial actions must be in compliance with other environmental and public health laws.

3) *Long-term effectiveness and permanence.* Analysis should focus on the residual risks that will remain at the site after completion of the remedial action. Consideration should be given to any long-term management requirements, the reliability of any necessary controls, and the potential need for replacement of the remedy.

4) *Reduction of toxicity, mobility, or volume.* The reduction potential of treatment methods should be compared in terms of magnitude, significance, and irreversibility. Persistence, toxicity, mobility, and bioaccumulation tendencies of any residuals must be considered.

5) *Short-term effectiveness.* The environmental impact of implementing a treatment must be evaluated, including the effectiveness and reliability of mitigative measures used to protect the health and welfare of workers and the community.

6) *Implementability.* The technical and administrative feasibility of treatment alternatives must be analyzed. Items such as seasonal constraints, availability of materials, equipment, or services, and operational reliability are all factors that must be weighed.

7) *Cost.* Cost considerations encompass all construction and operation and maintenance costs incurred over the life of the project. A remedy must be cost-effective in that its overall effectiveness is proportionate to its total costs.

8) *State acceptance*. Substantial and meaningful State involvement is a statutory requirement. States should be involved in all phases of the remediation process, including initiation, development, and selection of a remedial action.

9) *Community acceptance*. Although difficult to assess before the public hearings, consideration must be given to any issues that might concern the community. Groups specifically affected by a site have the statutory right to participate in the selection of a remedy.

These criteria fall into three groups: threshold, balancing, and modifying criteria. Protection of human health and the environment and compliance with applicable or relevant and appropriate requirements (ARARs) are threshold requirements that must be met. Long-term effectiveness and permanence; reduction of toxicity, mobility, or volume; short-term effectiveness; implementability; and cost are balancing factors used to weigh major tradeoffs between viable strategies. State and community acceptance are modifying considerations.

To complete the fourth step in the process, the lead agency must consider the advantages and disadvantages of each treatment alternative and balance the major tradeoffs to select the method that offers the best combination of attributes and is most appropriate for a given site. The proposed plan issued for public comment and review will identify the alternative selected, summarize the decision-making process, and allow for public participation.

The final phase of the remedial action process involves documenting the assessment (particularly how the nine criteria were used to select the remedy) and results in a record of decision (ROD).

Thus, the entire remedial action process follows the natural progression of investigation, analysis, and remediation, with the protection of human health and the environment kept foremost in all decisions.

Section 3
Technologies for In Situ Treatment

This section presents detailed information on specific in situ technologies that were selected for their potential or demonstrated ability to augment natural soil processes. The discussions are divided into the following treatment categories: soil flushing, solidification/stabilization, degradation, control of volatile materials, and physical and chemical separation techniques.

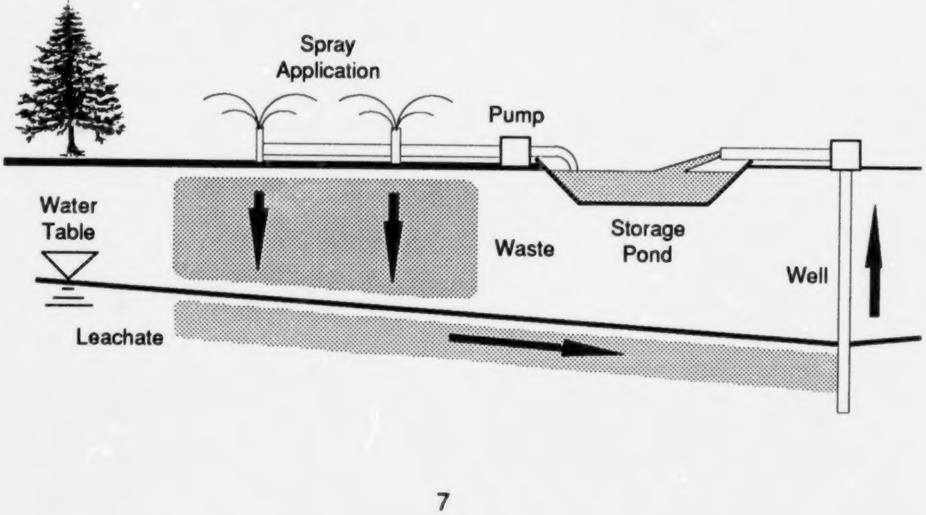
Remediation of hazardous waste sites can involve implementing several treatment technologies in series or what is called a treatment train. This approach may allow for a more comprehensive remediation than a single technology could provide. An example of this is product recovery by pumping free product to the surface, followed by soil flushing and pumping and treating on the surface, and subsequent in situ treatment of the residual materials by biodegradation.

3.1 Soil Flushing

The use of soil flushing to remove soil contaminants involves the elutriation of organic and/or inorganic constituents from soil for recovery and treatment. The site is flooded with the appropriate washing solution, and the elutriate is collected in a series of shallow wellpoints or subsurface drains. The elutriate is then treated and/or recycled back into the site. During the elutriation process, contaminants are mobilized into the flushing solution by way of solubilization, formation of emulsions, or a chemical reaction with the flushing solution (USEPA 1985). Collection of elutriate is required to prevent uncontrolled contaminant migration through uncontaminated soil and into receiver systems, including ground and surface waters. Figure 1 presents an example of a soil flushing system with elutriate recycling.

Flushing solutions may include water, acidic aqueous solutions (sulfuric, hydrochloric, nitric, phosphoric, and carbonic acid), basic solutions (e.g., sodium hydroxide), and surfactants (e.g., alkylbenzene sulfonate). Water can be used to extract water-soluble or water-mobile constituents. Acidic solutions are used for metals recovery and for basic organic constituents (including amines, ethers,

Figure 1. Schematic of an elutriate recycle system.



and anilines); basic solutions for metals (including zinc, tin, and lead); and basic solutions for some phenols, complexing and chelating agents, and surfactants (USEPA 1985).

The addition of any flushing solution to the system requires careful management and knowledge of reactions that may adversely affect the soil system. For example, a sodium addition as sodium hydroxide to soil systems may adversely affect soil permeability by affecting the soil sodium absorption ratio. It is not only important to understand the chemical reaction(s) between the solvent and solute, but also between the solvent and the site/soil system.

At a site contaminated by organic constituents, recycling the elutriate back through the soil for treatment by biodegradation may be possible. Proper control of the application rate, based on hazardous waste land treatment principles (USEPA 1983), would provide for effective in situ treatment at soil concentrations that would allow controlled biodegradation of the waste constituents. This approach could eliminate the need for separate processes for treatment and disposal of the collected waste solution, or at least provide for a combination of pretreatment/land application that may be considerably more economical than the use of unit operations alone for treatment of elutriate.

For soils contaminated with inorganic and organic constituents, a combination of pretreatment that reduces or eliminates the metal constituent(s) in the elutriate by precipitation, followed by a land application of the elutriate, may be a feasible cost-effective method of treatment.

Soil flushing and elutriate recovery may also be appropriate in situations where chemical oxidizing or reducing agents are used to degrade waste constituents chemically and result in the production of large amounts of oxygenated, mobile, degradation products. The most conservative and safest approach may be to flush the soil after treatment to recover and possibly to reapply the elutriate in a controlled manner to the soil surface.

Both inorganics and organics are amenable to soil flushing treatment if they are sufficiently soluble in an inexpensive solvent that can be obtained in large volumes. Surfactant can be used for hydrophobic organics. Studies have been conducted to determine appropriate solvents for mobilizing various classes and types of waste constituents. The characteristics of various surfactants and their environmental and chemical properties are listed in Table 1. Laboratory testing on site-specific soils should be undertaken to verify surfactant properties (Amdurer et al. 1986).

Success or failure also depends on the retention or inactivation of the solvent by the soil. The soil overlying the contaminated zone will need to be completely saturated before the solvent reaches the zone of contamination. The interaction of the solvent with the soil must be considered for successful application of the treatment.

The level of treatment that can be achieved will vary depending on the contact of the flushing solution with waste constituents, the appropriateness of the solutions for the wastes, the soil adsorption coefficients of the waste(s), and the hydraulic conductivity of the soil. This technology should produce the best treatment results in highly permeable soils with low organic content. Despite the varying level of treatment accomplished by soil flushing, however, once the waste components have been removed from the soil, results are not reversible and no retreatment is necessary.

3.1.1 Status of the Technology

Several bench- and pilot-scale studies have been completed on the effectiveness of extraction as an in situ treatment technology. Nash (1988) used soil flushing with surfactants to demonstrate contaminant reduction at the Volk Air National Guard Base in Camp Douglas, Wisconsin. The contamination consisted primarily as medium-weight oil (2,000-25,000 mg/kg) with some volatile organics (5 to 10 mg/kg). After applying surfactants on small areas of contamination at a rate of 77 L/m^2 per day for 7 days, no statistically significant reduction of contamination was observed. Nash concluded that in situ soil flushing with aqueous surfactants would be ineffective at sites that have contaminants with relatively high soil-sorption values ($K>10^{-3}$).

Table 1. Surfactant Characteristics*

Surfactant type		Selected properties and uses	Solubility	Reactivity
Anionic	1) Carboxylic acid salts	Good detergency	Generally water-soluble	Electrolyte-tolerant
	2) Sulfuric acid ester salts	Good wetting agents		Electrolyte-sensitive
	3) Phosphoric and polyphosphoric acid esters	Strong surface tension reducers	Soluble in polar organics	Resistant to biodegradation
	4) Perfluorinated anionics			High chemical stability
	5) Sulfonic acid salts	Good oil-in-water emulsifiers		Resistant to acid and alkaline hydrolysis
Cationic	1) Long-chain amines	Emulsifying agents	Low or varying water solubility	Acid-stable
	2) Diamines and polyamines	Corrosion inhibitor		
	3) Quaternary ammonium salts		Water-soluble	Surface adsorption to silicaeous materials
	4) Polyoxyethylenated long-chain amines			
Nonionic	1) Polyoxyethylenated alkylphenols alkylphenol ethoxylates	Emulsifying agents	Generally water-soluble	Good chemical stability
	2) Polyoxyethylenated straight-chain alcohols and alcohol ethoxylates	Detergents	Water-insoluble formulations	Resistant to biodegradation
	3) Polyoxyethylenated polyoxypropylene glycols	Wetting agents		Relatively nontoxic
	4) Polyoxyethylenated mercaptans	Dispersents		
	5) Long-chain carboxylic acid esters	Foam control		Subject to acid and alkaline hydrolysis
	6) Alkylamine "condensates", alkanolamides			
	7) Tertiary acetylenic glycols			
Amphoterics	1) pH-sensitive	Solubilizing agents	Varied (pH-dependent)	Nontoxic
	2) pH-insensitive	Wetting agents		Electrolyte-tolerant
				Adsorption to negatively charged surfaces

* Source: Amdurer et al. 1986.

Dworkin et al. (1988) indicate that in situ soil flushing, in combination with a biodegradation process, could be a cost-effective means of soil remediation at sites contaminated with creosote. Specifically, soil flushing may be used to remove high concentrations of the polycyclic aromatic hydrocarbons associated with creosote contamination, and the process may be followed by in situ biodegradation. They report that this system of flushing/biodegradation would result in significant reduction or possibly elimination of the health risks and environmental impacts associated with the migration of PAHs into ground water and surface water.

Kuhn and Piontek (1989) proposed using in situ soil flushing combined with biodegradation to remediate a contaminated wood-preserving site. During screening tests to determine a potentially effective combination of alkaline agents, polymers, and surfactants for treatment, several combinations were discovered to be effective for the site-specific remedial action necessary. As a final test, flood tests were conducted on soil cores to select the most effective combination of polymer, alkaline agents, and surfactants and to predict the degree of contaminant removal potentially achievable with the combination. In the laboratory testing, 98 percent contaminant removal was achieved on the core samples representing ideal field conditions. Based on the results of the testing program, in situ soil flushing followed by in situ biodegradation was determined to be a cost-effective method of site remediation.

Soil flushing has been used to effect several full-scale remedial actions. Truett et al. (1982) reported the use of water flushing for 5 to 6 years to reclaim a former herbicide factory site in Sweden. A wellpoint collection and recharge system was installed at the Goose Farm Site, Plumstead, New Jersey (USEPA 1984). Water was used to flush the contaminants from the soil. Bench-scale leaching tests indicated that 10 complete soil rinses (1.1 x 10 gallons of water) would be required for complete soil flushing of total organic carbon (TOC) to acceptable levels. Operations were terminated before completion; approximately 7.8 x 10 gallons of water had been processed. Concentrations of TOC in the contaminated area averaged approximately 3300 ppm in the ground water after treatment (initial TOC concentrations ranged from 1,600 to 17,000 ppm).

Water was again used as the flushing solution for cleanup of a tetrachloroethylene spill in Germany (Stief 1984). A 50 percent decrease in tetrachloroethylene over an 18-month period was achieved. The leaching fluid and polluted ground water were pumped out of eight wells and treated in an activated carbon filter. The treated water was used for further leaching, and within 18 months, 17 metric tons of hydrocarbons were recovered.

3.1.2 Secondary Impacts

The solutions used for the flushing may themselves be potential pollutants; they may have toxic and other environmental impacts of the soil system and water receiver systems. The soil system after treatment is altered from its original state. Its physical, chemical, and biological properties may be altered adversely (e.g., the pH may be lowered by the use of an acidic solvent) or the soil may be compacted as a result of being flooded. These soil properties may have to be restored to assure that other treatment processes can occur (e.g., biodegradation).

A potential exists for the flushing solvent to transport contaminants into an underlying aquifer. In almost all cases where extraction technologies are used, it is imperative that the ground-water flow rate and direction are fully understood before solvents are applied to the contaminated area. Also, withdrawal wells with sufficient capacity to draw all solvent/contaminant solutions to the surface for treatment are necessary.

3.1.3 Equipment, Exogenous Reagents, and Information Required

Equipment used for soil flushing includes drains and a collection and distribution system. Reapplication of collected elutriate also may necessitate the construction of a holding tank for the elutriate. Solvents for flushing are required.

The following information is needed for application of this in situ treatment:

- Characterization and concentration of waste constituents.
- Depth, profile, and areal distribution of contamination.
- Partitioning of waste constituents between solvent(s) and soil.
- Effects of washing agent (solvent) on physical, chemical, and biological properties of soil.
- Suitability of site for flooding and installation of wells or subsurface drains.
- Site-specific ground-water flow rate and direction.
- Trafficability of soil and site.

3.1.4 *Advantages of Soil Flushing*

Advantages of using this treatment technology for site remediation include:

- Removal of contaminants is permanent, no additional treatments are necessary if the soil flushing process is successful.
- The technology is easily applied to permeable soils.
- Costs are moderate, depending on the flushing solution chosen.

3.1.5 *Disadvantages of Soil Flushing*

Disadvantages of using soil flushing are as follows:

- The technology introduces potential toxins (the flushing solution) into the soil system.
- Physical/chemical properties of the soil system may be altered because of the introduction of the flushing solution.
- A potential exists for solvents to transport contaminants away from the site into uncontaminated areas.
- A potential exists for incomplete removal of contaminants due to heterogeneity of soil permeability.

3.2 Solidification and Stabilization

Solidification and stabilization refer to treatment processes that are designed to accomplish one or more of the following:

- Improve handling and physical characteristics of the waste by producing a solid from liquid or semiliquid wastes.
- Reduce contaminant solubility in the treated waste.
- Decrease the exposed surface area across which transfer or loss of contaminants may occur.

Solidification techniques eliminate the free liquid, increase the bearing strength, decrease the surface area of the waste material, and produce a monolithic solid product of high structural integrity. Solidification may involve encapsulation of fine waste particles (microencapsulation) or large blocks of wastes (macroencapsulation). Chemical interactions do not necessarily occur between the wastes and the solidifying agents, but the waste material is mechanically bound within the solidified matrix in such a way that the release rate of hazardous substances is significantly decreased upon exposure to air, water, soil, or mild acidic conditions.

Stabilization refers to the process of reducing the hazardous potential of waste material by converting the contaminants into their least soluble, mobile, or toxic form. This technique does not necessarily change the physical characteristics of the waste.

3.2.1 Solidification/Stabilization Techniques

Solidification/stabilization techniques have been widely used in low-level radioactive waste disposal. Their application to hazardous wastes is becoming more common, however, and many vendors are studying and developing processes that are directly applicable to hazardous waste-contaminated soils and sludges. Table 2 identifies several in situ applications of this technology.

Waste solidification/stabilization systems that are potentially useful in remedial action activities are as follows:

- Pozzolan-portland cement systems
- Lime-fly ash pozzolan systems
- Thermoplastic microencapsulation
- Sorption
- Organic binding

Cullinane et al. (1986) describe the first four of the systems as follows:

- Pozzolan-portland systems used portland cement and pozzolan materials (e.g., fly ash) to produce a structurally stronger waste/concrete composite. The waste is contained in the concrete matrix by microencapsulation (i.e., physical entrapment).
- Lime-fly ash pozzolanic processes use a finely divided, noncrystalline silica in fly ash and the calcium in lime to produce low-strength cementation. The waste containment is produced by microencapsulation in the pozzolan concrete matrix.
- Thermoplastic microencapsulation involves blending fine particulate waste with melted asphalt or other matrix. Liquid and volatile phases associated with the wastes are driven off, and the wastes are isolated in a mass of cool hardened asphalt.
- Sorption involves adding a solid to soak up any liquid present. The major use of sorption is to eliminate all free liquid. Typical examples of nonreactive, nonbiodegradable sorbents are activated carbon, clays, zeolites, anhydrous sodium silicate, and various forms of gypsum.

Many of these additives are not effective in immobilizing organic contaminants. Recent studies, however, indicate that modified clays can be used to immobilize organic contaminants (Gibbons and Soundararajan 1988). Clay particles are platy-shaped minerals that have negative charges on their surfaces as a result of isomorphous substitution. To achieve neutrality in their structure, clay particles attract cationic metals such as Li^+, Na^+, Ca^+, and Mg^+ on their surfaces. These cations might be further replaced by quarternary ammonium ions such as $[R_4N\ ]$. Introduction of these organic cations into clays increases the interplanar distance between the clay particles and provides more suitable conditions for bonding of organic contaminants (Gibbons and Soundararajan 1988).

An extensive discussion of these and other solidification/stabilization techniques is presented in the document entitled "Handbook for Stabilization/Solidification of Hazardous Wastes" (Cullinane et al. 1986). Also, Malone et al. (1979 and 1980) present detailed information concerning the solidification/stabilization of hazardous wastes. Physical and chemical testing and technology evaluation procedures are discussed in another report (PEI Associates, Inc. and Earth Technology Corp. 1989).

The most significant challenge in applying solidification/stabilization treatment in situ for contaminated soils is achieving complete and uniform mixing of the solidifying/stabilizing agent with the soils. In situ mixing of solidifying/stabilizing agents with contaminated sludges in a lagoon is typically

Table 2. Selected In Situ Solidification Case Studies*

Site/ contractor	Contaminant (concentration)	Treatment volume, cubic yards (except as noted)	Physical form	Pretreat	Binder	Percentage binder(s) added	Treatment	Disposal	Volume increase, %	Scale of operation
Midwest, U.S. Plating Co., Envirite	Cu, Cr, Ni	16,000	Sludge	No	Portland cement	20	In situ	On site	>0	Full-scale
Unnamed, ENRECO	Pb/soil (2-100 ppm)	7,0	Solid/ soils	No	Portland cement and proprietary	Cement (15-20) proprietary -5	In situ	Landfill	Mass >20 (volume >30-35)	Full-scale
Hialea, FL, Geo-Con, Inc.	PCBs (0.800 ppm)	300 (7,000 total)	Wet soil	No	HWT-20TM (cement-based)	15	In situ	On site	>Small	Pilot (full-scale planned)
Unnamed, Kentucky, ENRECO	Vinyl chloride ethylene dichloride	180,000	Sludges, variable	Yes	Portland cement and proprietary	Varied 25+	In situ	On site (two secure cells built on site)	>7-9	Full-scale
N.E. Refinery, ENRECO	Oil sludges, Pb, Cr, As	100,000	Sludges, variable	No	Kiln dust (high CaO content)	Varied, 15-30	In situ	On site	>Varied, ~20 average	Full-scale
Velsicol Chem., Memphis Env. Centre	Pesticides and organics (resins, etc.) up to 45% organic	20,000,000 gallons	Sludges, variable	No	Portland cement and kiln dust, proprietary	Varied (cement 5-15)	In situ	On site	>Varied ~10 or less	Full-scale
Vickery, OH, Chemical Waste Management	Waste acid PCBs (<500 ppm), dioxins	235,000	Sludges (viscous)	Yes	Lime and kiln dust	15 CaO 5 kiln dust	In situ	On site (TSCA cells)	>-9+	Full-scale
Wood Treating, Savannah, GA, Geo-Con, Inc.	Creosote wastes	12,000	Sludges	Yes	Kiln dust	20	In situ	On site (lined cells)	>-14	Full-scale
Metalplating, WI, Geo-Con, Inc.	Al (9500 ppm) Ni (750 ppm) Cr (220 ppm) Cu (2000 ppm)	3,000	Sludges	No	Lime	25-Oct	In situ	On site landfill	>4-10	Full-scale

*Source: PEI Associates, Inc. and Earth Technology Corp. 1989 accomplished by use of a backhoe, clamshell, or dragline (Cullinane et al. 1986). Depending on the depth of contamination, however, these implements may not be useful for mixing in the subsurface.

This factor becomes more significant when multiple-constituent wastes have been buried and intermixed with soils of various textures and properties. Uniformity of the waste-reagent matrix is also important when the waste constituents are directly involved in the chemical reactions of the solidification/stabilization process (e.g., water required for the hydration process in portland cement-pozzolanic reactions) or when more than one additive is being used in the treatment of the wastes. Proper mixing or degree of contact between the waste, soil, and solidification/stabilization reagent depends on the following parameters (Truett et al. 1983):

- Viscosity of the agent.
- Permeability of the waste materials and the soils surrounding them.
- Porosity of the waste materials and soils.
- Special distribution of the wastes in the surrounding material (i.e., soils, rocks).
- Rate of reactions.

Truett et al. (1983) describe three methods for applying solidifying/stabilizing agents to the subsurface:

- *Injection method.* Solidifying/stabilizing agents can be injected into the waste material in liquid or slurry form. Injection can be achieved by flow of the solidifying/stabilizing reagent inside a porous tube to the required depth.
- *Surface application.* When the waste material is sufficiently shallow and permeable, stabilizing agents can be applied in a solid or liquid form onto the surfaces and allowed to penetrate. This application technique is especially appropriate for rendering a specific waste component less toxic. This method is not commonly used, however.
- *Application of electrical energy.* Electrical energy can be applied to the ground to melt the soils and rocks that contain hazardous material. This method involves the application of the electrical energy through electrodes placed into the ground to increase the temperature of the landfill material above the fusion point and to stabilize the waste components. A thin layer of graphite is usually placed between the electrodes to act as a starter to melt the soil. Before this process is applied, a cover may be placed over the fused area to capture the released gases during the process and to direct them to the treatment unit.

3.2.1.1 Status of the Technology

An in situ solidification/stabilization process involving a proprietary solidifying/stabilizing agent and a unique mixing system has been evaluated through the SITE Program (USEPA 1988). The proprietary agent, developed by International Waste Technologies (IWT), is claimed to bind with ions and neutral organics present in the soil and eventually to form macromolecules. The method for injecting the chemical into the soil, which was developed by Geo-Con, Inc., utilizes a hollow drill with an injection point at the bottom of the shaft. The drill is advanced into the ground to the desired depth. The chemical additive is then injected at low pressure to prevent excessive spreading and is blended with the soil as the drill rotates. The treated soil forms a solid vertical column. Soil columns overlap to insure that all the soil is adequately treated. The soil surface may then be covered with a layer of asphalt to protect the solidified mass from rain and water erosion. The technology was evaluated on PCB-contaminated soils at the General Electric Superfund Site in Hialeah, Florida. Two test sectors, 10 x 20 ft, were remediated to a depth of 18 ft in one sector and 14 ft in the other. Samples of untreated and treated soil were taken from the same locations in each test sector, and laboratory analyses were performed to obtain a comparison of physical properties and contaminant mobilities before and after soil treatment. The results are summarized here (USEPA 1989):

- Based on TCLP analyses, the PCBs appear to be immobilized. Because the PCB concentrations measured in the soil and leachates were very low, this finding was not conclusive.
- The physical test results were satisfactory (except for the freeze/thaw tests) which indicates a potential for long-term durability of the hardened mass. The results were as follows:
  - High unconfined compressive strength (average about 410 psi).
  - Treatment improved soil permeability four orders of magnitude, to an average of 4×10^{-7} cm/s.
  - Wet/dry weathered samples showed satisfactorily low weight losses.
  - Treatment increased volume by 8.5 percent.
  - Freeze/thaw weathered samples showed unsatisfactorily large weight losses.
  - Microstructural studies showed the treated soil to have a dense, homogeneous structure of low porosity, which might give long-term durability.

3.2.1.2 Secondary Impacts

The permeability of the treated area is significantly reduced and could prohibit subsequent use of the area for construction or revegetation. Runoff controls may be required.

3.2.1.3 Equipment, Exogenous Reagents, and Information Required

The equipment required for preparing, mixing, and applying solidification/stabilization reagents depends on the reagent, the process, and the depth of contamination. Application methods were discussed previously.

Knowledge of the waste composition is required for the selection of the proper reagent to stabilize waste components. Such knowledge is also needed to determine whether waste constituents will interfere with the setup of the solidifying agents in different processes (i.e., crystallization, polymerization, gelling, adhesion, or other setting mechanisms). In addition, information regarding the characteristics of the soils and other geologic materials and the rates and directions of ground-water movement are essential for a good assessment of the applicability of each solidification/stabilization process. This information can be obtained by various established methods and sampling techniques (Fenn 1980). Table 3 provides a summary of the compatibility of selected waste types with different solidification/ stabilization techniques.

The reagents required depend on the particular solidification/stabilization process being implemented. For physical entrapment (microencapsulation), portland cement and a pozzolanic material such as fly ash are the principal reagents. Another microencapsulation technique involves the use of lime and fly ash. Asphalt or bitumen is used to effect thermoplastic microencapsulation. For sorption processes, the adsorbents can include activated carbon, clays, zeolites, anhydrous sodium silicate, or gypsum. Organophilic clays and portland cement are necessary for binding of organic contaminants.

Table 3. Compatibility of Selected Waste Categories With Different Stabilization/Solidification Techniques*

Waste component	Treatment type Cement-based	 Pozzolan-based	 Thermoplastic microencapsulation
Organics			
Organic solvents and oils	May impede setting, may escape as vapor.	May impede setting, may escape as vapor.	Organics may vaporize on heating.
Solid and organics e.g., plastics, resins, tars)	Good--often increases durability.	Good--often increases durability.	Possible use as binding agent in this system
Inorganics			
Acid wastes	Cement will neutralize acids.	Compatible, will neutralize.	Can be neutralized before incorporation.
Oxidizers	Compatible	Compatible	May cause matrix breakdown, fire.
Sulfates	May retard setting and cause spalling unless special cement is used.	Compatible	May dehydrate and rehydrate, causing splitting.
Halides	Easily leached from cement, may retard setting.	May retard set, most are easily leached.	May dehydrate and rehydrate.
Heavy metals	Compatible	Compatible	Compatible
Radioactive materials	Compatible	Compatible	Compatible

*Source: Malone et al. 1980.

3.2.1.4 Advantages of Solidification/Stabilization

The advantages of this treatment technique are as follows:

- Additives and reagents are widely available and relatively inexpensive.
- The resulting solidified material may require little or no further treatment if proper conditions are maintained.
- Leaching of contaminants is greatly reduced.

3.2.1.5 Disadvantages of Solidification/Stabilization

The disadvantages of this treatment technology are as follows:

- Volume of treated material may increase with the addition of reagents.
- Delivering reagents to the subsurface and achieving uniform mixing and treatment in situ may be difficult.
- Volatilization and emission of volatile organic compounds may occur during mixing procedures.

3.2.2 In Situ Vitrification

In situ vitrification is a thermal treatment process by which contaminated soils are converted into chemically inert and stable glass and crystalline materials (Fitzpatrick et al. 1987). Field application requires the insertion of large electrodes into contaminated soils containing significant levels of silicate material and the generation of heat (up to 3600°C) by passing electric current through the electrodes. Because dry soils are not electrically conductive, a layer of flaked graphite and glass frit is placed between the electrodes; this transfers electrical energy and acts as a starter to increase the temperature of the soil and waste material. At this temperature, any soil or rock components of the waste material will melt (melting temperature of soils is 2000° to 2500°F), organic compounds will be pyrolyzed in the glass matrix, and many metallic materials will either fuse or vaporize. Any gases and vapors produced can be collected by placing a hood above the treating area to draw them for further treatment (Fitzpatrick 1988). After the process is terminated and the ground has been cooled, the fused waste material will be dispersed into a chemically inert and stable crystalline form that has very low leachability rates and almost the same chemical stability of granite. Figure 2 presents different processing stages of in situ vitrification techniques.

Figure 2. The in situ vitrification operating sequence.

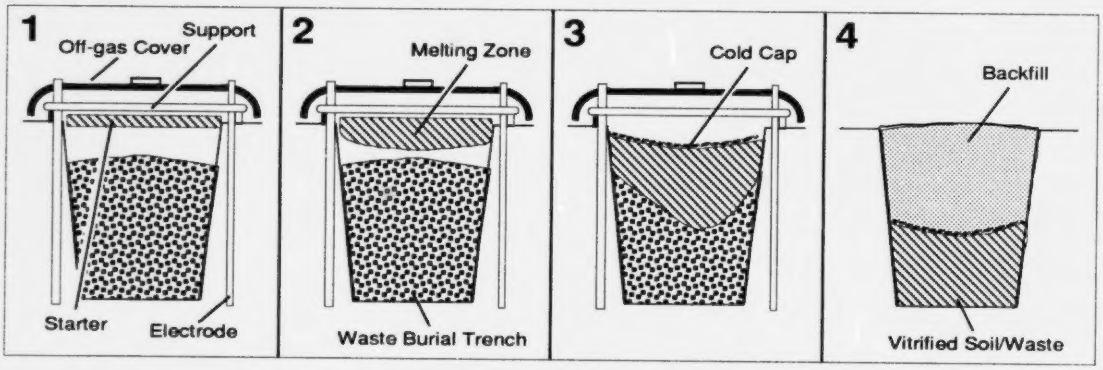


Table 4 presents the different scales of testing conducted in the development of the in situ vitrification technique (Fitzpatrick et al. 1987). The in situ vitrification technique was originally used to stabilize radioactive wastes, and it has only recently has been considered for the treatment of hazardous material. The process destroys nitrates and partially decomposes sulfate compounds in the wastes. Fluoride and chloride compounds are dissolved into the glass materials up to their limits of solubility (PEI 1988). Wastes containing heavy metals, PCBs, process sludges, and plating wastes are amenable to treatment by this vitrification process.

Table 4. In Situ Vitrification Test System Characteristics*

System scale	Power, kW	Electrode spacing, ft	Vitrified mass per setting	Number of tests
Bench	10	0.36	2 to 5 lb	5
Engineering	30	0.75 to 1.2	0.05 to 1.0 ton	26
Pilot	500	4.0	10 to 50 tons	15
Large	3750	11.5 to 18.0	400 to 800 tons	5

*Source: Fitzpatrick 1988

3.2.2.1 Status of the Technology

To date, no Superfund site has been treated by this technology in the field.

3.2.2.2 Secondary Impacts

The resulting vitrified mass is effectively inert and impermeable; therefore, it could not support vegetative growth unless covered by fill and topsoil.

3.2.2.3 Equipment, Exogenous Reagents, and Information Required

Operation of the in situ vitrification process requires an adequate power supply. A full-scale, four-electrode system requires a 4160-volt, 3000-kW source provided by a multitap transformer (Johnson and Cosmos 1989). Glass frit and graphite are necessary as starter materials for the melting processs. An off-gas hood is required for the entire treatment area. Off-gas treatment equipment may include quenchers, tandem nozzle scrubbers, separators, condensers, or high-efficiency particulate air (HEPA) filters.

Soil moisture is an important factor in the operation of the in situ vitrification process. More power and time are required to evaporate the water as soil moisture increases. Engineered barriers may be required to vitrify soils below the water table.

3.2.2.4 Advantages of In Situ Vitrification

The potential advantages of this technology are as follows:

- This process eliminates excavation, processing, and reburial of the hazardous compounds.
- The process minimizes exposure to contaminants.
- The process produces glassified materials that are long-lasting and highly durable.
- The treatment efficiency rate is relatively high (3 to 5 tons/h).
- Additives are relatively inexpensive.
- The products of this process have an extremely low leach rate (USEPA 1985).

3.2.2.5 Disadvantages of In Situ Vitrification

The potential disadvantages of this technology are as follows:

- The process is energy-intensive and often requires temperatures up to 2500°F for fusion and melting of the waste-silicate matrix.
- Special equipment and trained personnel are required.
- Water in soils affects operational time and increases the total cost of the process.
- The technology has the potential to cause contaminants to migrate to the outside boundaries of the treatment area instead of to the surface for collection.

3.3 Degradation

3.3.1 Chemical Degradation

Chemicals naturally undergo reactions in soil that may transform them into more or less toxic products or that may increase or decrease their mobility within the soil system. Chemical treatment of contaminated soils entails the reaction of pollutants with reagents, which results in products that are less toxic or that become immobilized in the soil column. These reactions are classified as oxidation reactions, reduction reactions, and polymerization reactions.

3.3.1.1 Chemical Oxidation

In general, chemical oxidation entails the loss of electrons by an atom or group of atoms. A broader definition of oxidation entails an increase in oxidation number of one reactant accompanied by a corresponding decrease in oxidation number of the other (reduced) reactant. Adding oxygen to a simple alkene (e.g., ethene) entails oxidation because electrons from ethene are "lost" to the oxygen atom. Oxidation reactions can occur within the soil matrix, and the rate of such reactions can be increased through management of the natural processes in a soil or through the addition of an oxidizing agent to the soil-waste complex. Certain compounds are more susceptible to oxidation than are others. The rate of oxidation depends on several factors, including temperature, oxygen concentration in the liquid, impurities present, and the concentration and chemical properties of the oxidizable component.

The following discussion primarily concerns the chemical oxidation of organics. Oxidation of heavy metals usually is not effective as a treatment method because the higher the oxidation state, the more mobile the heavy metal tends to be. Two approaches are applicable to in situ oxidation of hazardous waste materials in contaminated soils: 1) soil-catalyzed reactions, and 2) the addition of oxidizing agents.

The following information is required prior to the implementation of in situ treatment techniques for soil oxidation:

- Characterization and concentration of wastes, particularly organics at the site.
- Potential for oxidation of waste constituents (half-potentials, $E_{1/2}$).
- Oxidation products (particularly hazardous products).
- Solubility of organics.
- Depth, profile, and areal distribution of contamination.
- Soil moisture.
- Soil type and profile.
- Catalysts for oxidation present in soil.
- Trafficability of soil and site.

Soil-Catalyzed Reactions

Iron, aluminum, trace metals within layered silicates, and adsorbed oxygen have been identified as catalysts that promote free-radical oxidation of constituents in soil systems (Page 1941, Solomon 1968, Theng 1974, Furukawa and Brindley 1973, and Hirschler 1966). General characteristics of the organic chemicals likely to undergo oxidation include 1) aromaticity, 2) fused ring structures, 3) extensive conjugation, and 4) ring substituent fragments.

For oxidation to occur in soil systems, the redox potential of the solid phase must be greater than that of the organic chemical contaminant. Therefore, the half-cell potentials, $E_{1/2}$, of chemical contaminants need to be below the redox potential, 0.8V of a well-oxidized soil (Dragun and Baker 1979).

Another characteristic that is significant with respect to soil-catalyzed oxidation is the solubility of the organic contaminant. The oxidation reaction site is the hydrophilic clay mineral surface, and sorption to the surface precedes soil-catalyzed oxidation. Therefore, highly water-soluble compounds should be readily oxidized in clay-catalyzed systems.

Organic wastes that are water-soluble and have half-cell potentials below the redox potential of a well-oxidized soil are amenable to this treatment. Table 5 lists chemicals that do not undergo free-radical oxidation at soil and clay surfaces. This group of chemicals includes the aliphatic class of compounds.

Table 5. Some Chemicals That Do Not Oxidize At Soil And Clay Surfaces*

Chemical Name	
Acetamide	ß-Carotene
Acetone, anisilidene-	Cyclohexylamine
-, dianisilidene-	Monoethanolamine
-, dicinnamylidene-	Triethylamine
-, dibenzylidene-	

*Source: Dragun and Helling 1982.

The water content of the soil (degree of saturation) also may play an important role in controlling, and therefore managing, soil-catalyzed oxidation. Greater oxidation of chemical contaminants is expected in less-saturated soils (Dragun and Helling 1982). Therefore, the technique for immobilization by control of soil moisture is completely compatible with this treatment technique.

Immobilization techniques that involve controlling soil moisture or incorporating or adding uncontaminated soil should not only augment sorption, but should also augment clay-catalyzed reactions in the soil B-horizon where the clay fraction of soil is predominant. Thus, a physical-chemical and biological treatment system may be used in a layered system through the soil where sorption of hydrophobic constituents occurs in the upper soil layers or where organic matter content is high, and where chemical reactions for hydrophilic constituents occur in lower soil layers where the clay fraction predominates. Biological activity may be expected to increase the extent of degradation of constituents as the retention time of constituents is increased through sorption.

Hydrolysis refers to the reaction of water with an organic or inorganic compound where a hydrogen atom, an oxygen atom, and/or a hydroxide group from the water is incorporated into the products that result from the reaction:

$$\text{R-X} + H_2O \longrightarrow \text{R-OH} + \text{HX} \tag{3-1}$$

where R is the organic moiety and X is the leaving group.

Hydrolysis reactions are influenced by pH, temperature, degree of sorption, and the presence of other compounds that might act as catalysts. The rate of hydrolysis can be increased up to one order of magnitude for a change of 1 standard unit in pH (Amdurer et al. 1986). Hydrolysis of parathion occurs rapidly in alkaline solution at a pH value greater than 9. The hydrolysis rate also increases with increasing temperature.

Generally, organophosphorus pesticides and carbamate pesticides can be degraded by hydrolysis under alkaline conditions. Malathion, parathion, methyl parathion, 2,2-dichlorovinyl dimethyl phosphate, and carbaryl have been degraded by alkaline hydrolysis. Dimethoate, another organophosphorus pesticide, can be destroyed by alkaline hydrolysis, but the toxicity of mercaptoacetic acid, one of the reaction products, is almost as great as that of dimethoate itself (Tucker and Carson 1985).

Classes of compounds with potential for in situ treatment by hydrolysis include esters, amides, carbamates, phosphoric and phosphonic acid esters, and pesticides.

If required, clay may be applied to the soil surface and thoroughly incorporated through the depth of contamination. Drainage systems may have to be installed on the site to reduce soil moisture. Tillage may be used to dry and aerate the soil. Increasing soil temperatures may enhance soil drying and increase the rate of reaction. This treatment technology requires aerobic soil conditions to be maintained, which may be easy or difficult, depending on the site and the depth of contamination as it affects the ability to incorporate clays.

The level of treatment achievable will vary, depending on the oxidation potential of the waste constituents and the aeration of the soil.

Status of the Technology. Soil-catalyzed oxidation reactions have been verified in the field for several chemical classes, including s-triazines and organophosphate compounds. Some other compounds have been verified in the laboratory.

A site near Phoenix Arizona, contaminated with parathion was treated in situ. Laboratory and field feasibility studies showed that the combination of sodium hydroxide and water degraded ethyl and methyl parathion quickly by alkaline hydrolysis (King et al. 1985). Concentrations of the ethyl parathion were decreased by more than 50 percent in 15 days, and 76 percent after 69 days. Concentrations of methyl parathion decreased more rapidly; 81 percent after 15 days and 98 percent after 69 days.

Secondary Impacts. Drainage systems may have to be installed on the site to reduce soil moisture. Because tillage may be needed to dry and aerate the soil, wind erosion could occur.

Equipment, Exogenous Reagents, and Information Required. Equipment may be needed to set up a drainage system. If clay is added, applicators and tillers will be required to incorporate the clay. The information required prior to implementation is the same for all in situ treatment techniques for soil oxidation.

Advantages of Soil-Catalyzed Reactions. The advantages of soil-catalyzed oxidation reactions are as follows:

- Organophosphorus pesticides and carbamate pesticides can be degraded by hydrolysis under alkaline conditions.
- The process has been verified in the field for several chemical classes, including s-triazines and organophosphate compounds.
- Toxic concentrations may also be reduced by attenuation with the added soil.

Disadvantages of Soil-Catalyzed Reactions. The disadvantages of this process are as follows:

- Oxidation of the waste can produce substances more problematic than the parent compounds in the waste.
- Decreased soil moisture could result in retardation of microbial activity or increased ventilization of volatile waste constituents. (Volatilization may present a public health hazard, but it also may reduce toxic concentrations to soil microorganisms.)

- Depth of treatment may be limited by feasible depth of tillage.
- Tillage may increase the susceptibility of the soil to erosion.

Addition of Oxidizing Agents

Oxidizing agents can be used to degrade organic constituents in soil systems. The application of oxidizing reactions is usually limited because of their substrate specificity and pH dependence. Two powerful oxidizing agents considered for in situ treatment are ozone and hydrogen peroxide. The relative oxidizing ability of these chemicals compared with that of other well known oxidants is shown in Table 6. A serious potential limitation to the use of oxidizing agents for soil treatment is the additional consumption of the oxidizing agent(s) by nontarget constituents in the soil organic matter.

Table 6. Relative Oxidation Power of Oxidizing Species*

Species	Oxidation potential volts	Relative oxidation power
Fluorine	3.06	2.25
Hydroxyl radical	2.80	2.05
Atomic oxygen	2.42	1.78
Ozone	2.07	1.52
Hydrogen peroxide	1.77	1.30
Perhydroxyl radicals	1.70	1.25
Hypochlorous acid	1.49	1.10
Chlorine	1.36	1.00

*Source: Rice 1981

Ozone is an oxidizing agent that may be used to degrade recalcitrant compounds directly, to create an oxygenated compound without chemical degradation, or to increase the dissolved oxygen level in water for purposes of enhancing biological activity. Ozone is a colorless gas characterized by a pungent odor and very high oxidation potential. It cannot be shipped or stored; therefore, it must be generated on site prior to application. Ozone rapidly decomposes, and its half-life in ground water is only 18 minutes (Sanning and Black 1987).

The rate of decomposition of ozone is strongly influenced by pH. Ozone reactions are believed to be of two fundamental types: 1) direct reaction of ozone with the organic compounds; and 2) free radical reaction of ozone, which involves a hydroxyl free-radical intermediate. Direct reaction of ozone with solute achieves the most rapid decomposition of the solute. At high pH, the hydroxyl free-radical reactions tend to dominate over the direct ozone reactions. Thus, the relative rate of ozone reaction can be controlled by adjusting the pH of the medium.

If the specific organic constituents present in contaminated soil are relatively biodegradable, ozone treatment may be very effective as an enhancement of biological activity. If a large fraction of the matrix is relatively biorefractory, however, the amount of ozone required for direct treatment of the waste by chemical destruction will be a function of the organic matter present in the solution and in the soil; this will greatly increase the cost of treatment. The presence of natural soil organic matter will greatly increase the ozone dosage and consumption needed to treat the target constituents.

Ground water contaminated with oil products was treated with ozone to reduce the dissolved organic carbon (DOC) concentration (Nagel 1982). Dosages of 1 gram ozone per gram of dissolved organic carbon resulted in an ozone concentration of 0.1 to 0.2 ppm in the residual water. The treated water was then infiltrated into the aquifer through injection wells. The dissolved oxygen (DO) in the contaminated water increased. This increase in DO increased the microbial activity in the saturated soil zone, which stimulated microbial degradation of the organic contaminants. Ozone has also been used in the treatment of soils and ground water at the Karlsruhe site in Germany (Rice 1984).

Hydrogen peroxide is an oxidant that has been successfully used in wastewater treatment to degrade compounds that are resistant to biological treatment (recalcitrant). It has also been used to modify the mobility of some metals.

Hydrogen peroxide can react in three major ways:

1) Direct reaction with substrate as shown in Equation 3-2, where the peroxide reacts with silver nitrate to form elemental silver and nitric acid:

$$2AgNO_3 + H_2O_2 \longrightarrow Ag + O_2 + 2HNO_3 \qquad (3\text{-}2)$$

2) Can be degraded by UV light to form hydroxyl free radicals, as shown in Equation 3-3:

$$H_2O_2 + UV\ (2.53Å) \longrightarrow 2OH^{\cdot} \qquad (3\text{-}3)$$

3) Can undergo auto-decomposition in the presence of a metal catalyst, as shown in Equation 3-4.

$$6H_2O_2 \xrightarrow{\text{Metal}} 6H_2O + 3O_2 \qquad (3\text{-}4)$$

Hydrogen peroxide has also been used in conjunction with ozone to degrade compounds that are refractory to either material individually (Nakayama 1979).

Peroxide, as demonstrated in Equations 3-2 and 3-4, can be used to increase oxygen levels in the soil. In a previous study, Nagel (1982) found that increasing the oxygen content in soil/ground-water systems increased the microbial activity and microbial degradation of organic contaminants.

Because hydrogen peroxide is a strong oxidant, it is nonselective. If this material is added to the soil, it will react with any oxidizable material present in the soil. This is a major concern because the concentration of natural organic material in the soils may be lowered, which would result in a decrease in the sorption capacity of some organics.

Hypochlorite, generally available as potassium, calcium, or sodium hypochlorite, has never been used in the treatment of contaminated ground water or soils (Sanning and Lewis 1987). Tolman et al. (1978) described the conceptual design and in situ detoxification of cyanide with sodium hypochlorite. The reactions of many organics with hypochlorite result in the formation of chlorinated organics that can be equally or more toxic than the original contaminant.

Some hazardous compounds are known to be nonreactive with ozone. Nonreactive chemical species are usually inorganic compounds in which cations and anions are in their highest oxidation state, or organic compounds that are highly halogenated. No information currently exists concerning the susceptibility of many hazardous chemicals to ozone oxidation.

The following are some general rules concerning chemical destruction of organic constituents:

- Saturated aliphatic compounds that do not contain easily oxidized functional groups are not readily reactive with ozone. Examples include saturated aliphatic hydrocarbons, aldehydes, and alcohols.
- For aromatic compounds, reactivity with ozone is a function of the number and type of substituent(s). Generally, substituents that withdraw electrons from the ring deactivate the ring toward ozone. Examples are halogens, nitro, sulfonic acid, carbonyl, and carboxyl groups. Substituents that release electrons activate the ring toward ozone. Examples are alkyl, methoxyl, and hydroxyl.

The following general patterns have been identified with regard to reactivity with ozone:

1) Phenol, xylene > toluene > benzene

2) Pentachlorophenol < dichloro-, trichloro-, tetrachlorophenol

Ozonation of hazardous pesticides may actually be detrimental in many instances. Table 7 presents specific examples in which reactions of ozone with parent compounds result in the production of hazardous products that are often degraded very slowly by ozone.

Table 7. Hazardous Products of Ozone Reactions*

Parent compound	Reaction product	Oxidation of product with ozone
Aldrin	Dieldrin	Very slow
Heptachlor	Heptachlor epoxide	Stable to further oxidation
DDT	DDE	-
Parathion	Paraoxon	Nitrophenols, phosphoric acid
Malathion	Malaoxon	-

*Source: Sims and Bass 1984.

Hydrogen peroxide has been demonstrated to be effective for oxidizing cyanide, aldehydes, dialkyl sulfides, dithionate, nitrogen compounds, phenols, and sulfur compounds (FMC Corp. 1979).

The reaction of peroxide with many chemical classes increases the mobility of the products (Amdurer et al. 1986). Table 8 shows chemical groups that react with peroxides and form more mobile products.

Table 8. Chemical Groups That React With Peroxides To Form More Mobile Products*

Acid chlorides and anhydrides
Acids, mineral, nonoxidizing
Acids, mineral, oxidizing
Acids, organics
Alcohols and glycols
Alkyl halides
Azo, diazo compounds, hydrazine
Cyanides
Dithio carbamates
Aldehydes
Metals and metal compounds
Phenols and cresols
Sulfides, inorganic
Chlorinated aromatics/alicycles

*Source: Sims and Bass 1984.

Several oxidants for the treatment of PCB-contaminated wastes have been evaluated (Carpenter and Wilson 1988; Arienti et al. 1986) with the following results. Potassium permanganate plus chromic acid and nitric acid cannot destroy PCBs with 5 to 7 chlorine atoms per molecule. When chloroiodides are used, products of partial degradation may be toxic. No commercial application of this process exists. Additional bench-scale testing is needed for further optimization of the process, including the possibility of in situ decontamination of contaminated soil. Oxidation with ruthenium tetroxide (RuO_4) has been applied on a laboratory scale; however, the reaction end products from TCDD degradation have not been identified (Ayres et al. 1985).

The oxidizing agents may be applied in water solutions directly onto the soil surface, injected into the subsurface, or applied through injection wells, depending on the depth and location of contamination. Loading rates can be determined in short-term treatability studies.

Status of the Technology. A formaldehyde spill at Ukiah, California, was treated successfully by in situ chemical oxidation and biological treatment techniques. Alkaline hydrogen peroxide was used to lower the formaldehyde concentration to levels where biological oxidation could be used. At the end of two days, the concentration dropped from 30,000 to 50,000 ppm to about 500 to 1000 ppm. At this point, a biological treatment process was used, and one last peroxide treatment was applied at the end of the biological treatment after confirmation of <42 ppb residual formaldehyde. The purpose of this treatment was to sterilize the area. (Sikes et al. 1984).

Secondary Impacts. Oxidizing agents may result in violent reactions with certain classes of compounds (e.g., metals) and may be corrosive to application equipment. Their use may also affect soil hydraulic properties (e.g., infiltration rate), especially in structured soils. Oxidation of soil organic matter may decrease sorption sites for nonoxidizable waste constituents. Oxygenated degradation products are expected to be more polar than the parent compounds and therefore potentially more mobile. The chemical reaction may produce a large quantity of potentially mobile constituents in a relatively short period of time and necessitate the installation of recovery wells. The oxygenated products may also be toxic to soil systems, human health, and the environment. Some products may be more refractory than the parent compounds. The use of oxidizing agents may also increase the mobility of some metals.

Equipment, Exogenous Reagents, and Information Required. Power implements are required. If ozone is used, an ozone generator is necessary. Depending on the application method, an irrigation system, applicators, or injection wells may be needed. Exogenous reagents needed are oxidizing agents, ozone, or hydrogen peroxide. In addition to the general information requirements, the soil and water pH must be known, along with the selectivity of oxidizing agents for specific wastes present at the site.

Advantages of the Addition of Oxidizing Agents. The advantages of this technique are as follows:

- The achievable level of treatment is potentially high for wastes susceptible to oxidation, in soils that do not contain large quantities of competing oxidizable substances, and for limited areas of contamination.
- Oxidizing agents may have beneficial effects on microbial degradation processes by adding O_2 to the soil-water solution.

Disadvantages of the Addition of Oxidizing Agents. The disadvantages of this technique are as follows:

- The effectiveness of peroxide may be inhibited because it simultaneously increases mobility and decreases possible sorption sites.
- The reactions of many organics with hypochlorite results in the formation of chlorinated organics that can be equally or more toxic than the original contaminant.
- Presence of reduced Fe^{2+} in soil will lower the efficiency of the process because of oxidation.
- Ozonation of hazardous pesticides may actually be detrimental in many instances.
- Because ozone and hydrogen oxide are very strong oxidizers, they are not particularly discriminating in the substances they will oxidize in the soil. Thus, much of the oxidant will be wasted on oxidizing nontarget compounds.
- Treatment may have to be repeated if initial applications prove to be insufficient.

3.3.1.2 Chemical Reduction

Chemical reduction is a process in which the oxidation state of an atom is decreased. Reducing agents are electron donors, and reduction is accomplished by the addition of electrons to the atom. Reduction of chemicals may occur naturally within the soil system. Certain compounds are more susceptible to reduction than others because they will accept electrons. The addition of reducing agents to soil to degrade reducible compounds can be used as an in situ treatment technology.

Reducing agents and conditions of reduction vary with organics and with metals. The following discussion is divided into organics, chromium, and selenium for ease of organization of the information.

Information needed before the implementation of reduction technologies is as follows:

- Characterization and concentration of wastes, particularly organics at the site.
- Potential for reduction of waste constituents.
- Reduction products.
- Depth, profile, and areal distribution of contamination.
- Soil and waste pH.
- Soil moisture.
- Selectivity of reducing agent(s) for specific wastes present at the site.
- Trafficability of soil and site.

Addition of Reducing Agents to Treat Organic Chemicals

Chemical reduction through the use of catalyzed metal powders and sodium borohydride has been shown to degrade toxic organic compounds. Reduction with catalyzed iron, zinc, or aluminum effect treatment through mechanisms such as hydrogenolysis, hydroxylation, saturation of aromatic structures, condensation, ring opening, and rearrangements to transform toxic organics to innocuous forms. Reductive dehalogenation of a variety of chlorinated organics, unsaturated aromatics, and aliphatics has been demonstrated in laboratory studies in which catalyzed metal powders were used. The treatment reagents are costly, and the effectiveness of chemical reduction in soils has yet to be demonstrated (Sanning and Lewis 1987).

Catalyzed metal powders have been used successfully for aqueous solutions passed through beds of reactant diluted with an inert solid (Sweeney 1981). This process may be adaptable to terrestrial application; however, it has not yet been directly demonstrated. It has been used successfully on the following specific constituents:

Hexachlorocyclopentadiene
p-Nitrophenol
Trichloroethylene
Chlorobenzene
Kepone
PCBs
Chlordane
Chlorinated phenoxyacetic acid
Di-and tri-nitrophenols
Atrazine

Iron powders are not only preferred for soil systems, they are also the most cost-effective and readily available. Reactions of iron with some organic constituents are as follows:

Removal of halogen atom and replacement by hydrogen in halogenated organic species:

$$Fe + H_2O + RCl \rightleftharpoons RH + Fe^{2+} + OH^- + Cl^- \tag{3-5}$$

An example is the transformation of DDT to DDA.

Replacement of a halogen by a hydroxyl group:

$$Fe + 2H_2O + 2RCl \rightleftharpoons 2ROH + Fe^{2+} + 2Cl^- + H_2 \tag{3-6}$$

Saturation of an aromatic structure:

$$Fe + 2H_2O + RCH = CHR \rightleftharpoons RCH_2CH_2R + Fe^{2+} + 2OH^- \tag{3-7}$$

An example is the transformation of chlorobenzene to cyclohexanol.

Condensation of species:

$$Fe + 2RCl \rightleftharpoons RR + 2Cl^- + Fe^{2+} \tag{3-8}$$

An example is the condensation of DDT to TTTB.

Consumption of metal occurs through the preceding reactions and also through reactions of the active metal with water:

$$Fe + 2H_2O \rightleftharpoons Fe^{2+} + 2OH^- + H_2 \qquad (3\text{-}9)$$

The total consumption of metal from these reactions in aqueous solutions of industrial wastewaters produces 1 to 5 mg/L of metal (Fe^{2+}) in the solution when low toxicant levels are treated.

Organic chemical constituents in soil may also be chemically reduced through the use of sodium borohydride and zinc. These chemicals have been successful for in situ, small-scale, field experiments with soils (Staiff et al. 1981). Table 9 presents results of reductive treatment for degradation of paraquat in soil. The results indicate that sodium borohydride and powdered zinc/acetic acid combinations effectively degraded paraquat in soil and sand media. Toxic products and other byproducts that may result from reductive treatment were not investigated to any significant extent in this study.

Table 9. Chemical Reductive Treatment For Degradation of Paraquat In Soil*

Chemical treatment	Paraquat in soil, ppm Initial (1 day)	 4 months	Comment
None	9590	6300	-
NaBH4-soil	None detected	None detected	Violent foaming
NaBH4-sand	None detected	None detected	No foaming
Powdered Zn/ acetic acid	60	69	Some bubbling

*Source: Staiff et al. 1981.

The soil should not be disturbed prior to treatment so dilution of contaminants in the soil can be avoided. For metal-catalyzed powders, stoichiometric excess of the reducing powder should be applied to the soil surface and mixed with the contaminated soil to achieve maximum contact. For chemical reducing agents, a sodium borohydride stabilized water solution should be applied to the soil at 50 percent stoichiometric excess. A solution used in a small-scale study contained the following:

Sodium borohydride	12 ± 0.5%
Sodium hydroxide	42 ± 2%
Water	Balance

Iron may be more desirable than zinc or aluminum because it is naturally present in most soils. Aluminum is toxic to biological systems and contributes to soil acidity. The soil pH must be maintained at 6 to 8 for maximum treatment effectiveness. Soil water should be controlled at less than saturated conditions (60 to 80 percent of field capacity) to provide an aqueous environment in which reductive reactions can occur while leaching is prevented.

The achievable level of treatment is potentially high for wastes susceptible to reduction and for limited areas of contamination. If the soil contains large quantities of competing constituents susceptible to reduction, the level of treatment may be greatly decreased. If the reducing agents are not sufficient, treatment may have to be repeated because of high levels of naturally occurring reducible compounds in the soil.

Status of the Technology. In Phoenix, Arizona, a site contaminated with toxaphene was chemically treated with NaOH; the mechanism is believed to be dechlorination (King et al. 1985). An area of 1.7 acres was treated, and the site was tilled to a depth of 1.5 to 2.0 feet prior to cleanup. An irrigation system was installed, and 35,000 lb of sodium hydroxide was added to the soil. No change was noted in the concentration after 15 days; however, the average concentration decreased by 21 percent after 36 days and by 45 percent after 69 days. In situ treatment did not reduce toxaphene concentrations as well as the laboratory and field pilot studies did. After the Phase I chemical treatment, the site was prepared for the Phase II anaerobic treatment. Results are not yet available.

Fresh manure was applied to a soil-waste mixture (2 percent manure dry weight) contaminated with toxaphene to lower the redox potential of the soil (McLean et al. 1988). Toxaphene was collected from a site where spent toxaphene dipping solution used in cattle operations had been disposed of on the soil. The application of manure was not effective in stimulating degradation of the toxaphene residues over the time period of the study.

Secondary Impacts. The addition of reducing agents as a treatment for organics in soil may have the following secondary impacts:

- The use of reducing agents may also degrade soil organic matter.
- The products of reduction may present problems with respect to toxicity, mobility, and degradation.
- The addition of metals to soils adds to the metal contaminant load.
- The addition of metals with acetic acid could increase metal mobility by decreasing soil pH.
- Aluminum is toxic to biological systems and contributes to soil acidity.
- The addition of sodium borohydride may have an adverse impact on soil permeability.

Equipment, Exogenous Reagents, and Information Required. Power implements, tillers, and applicators are needed. Also needed is an irrigation and drainage system. Controls for run-on and runoff management may also be needed. The possible exogenous reagents include catalyzed iron, zinc, or aluminum and sodium borohydride. The information requirements are those listed for all reduction treatments.

Advantages of the Addition of Reducing Agents to Treat Organic Chemicals in Soil. The achievable level of treatment is potentially high for wastes susceptible to reduction and for limited areas of contamination.

Disadvantages of the Addition of Reducing Agents. The disadvantages of using this process for treating organic chemicals in soil are as follows:

- The treatment reagents are costly.
- The effectiveness of chemical reduction in soils has not yet been demonstrated.
- If soil contains large quantities of competing constituents susceptible to reduction, treatment may have to be repeated.

Addition of Reducing Agents to Treat Chromium

Hexavalent chromium is highly toxic and mobile in soils. Treatment consists of reducing Cr(VI) to Cr(III), which is less toxic and is readily precipitated by hydroxide over a wide pH range. In a study of the relative mobility of metals in soils at pH 5, Cr(III) was found to be the least mobile (Griffin and Shimp 1978).

Acidification agents (such as sulfur) and reducing agents (such as leaf litter, acid compost, or ferrous iron) may help to convert Cr(VI) to Cr(III) (Grove and Ellis 1980). Because hexavalent chromium itself is a strong oxidizing agent under acidic conditions, Cr(VI) will be readily reduced to Cr(III) even without the addition of strong reducing agents. After the reduction, liming of the soil will precipitate

Cr(III) compounds. Precipitation of Cr(III) occurs at pH 4.5 to 5.5, so little soil pH adjustment is necessary. Caution is required, however, because Cr(III) can be oxidized to Cr (VI) under conditions prevalent in many soils; e.g., under alkaline and aerobic conditions in the presence of manganese.

Acidification requirements for a particular soil need to be determined. Three moles of ferrous sulfate will reduce one mole of Cr(VI). More than this amount will probably be needed to account for other reduction reactions occurring in the soil. The quantity of organic material cannot be predicted from stoichiometric considerations. After the acidification and reducing steps, liming materials are applied to raise the pH to greater than 5.

Leaf litter and compost are easily applied to soils by standard agricultural methods if site/soil trafficability is suitable. Ferrous sulfate may be applied directly to the soil or through an irrigation system. Reduction of Cr(VI) must occur under acidic conditions and be followed by liming to precipitate Cr(III). Acidification and liming are standard agricultural practices.

The pH of the system must be maintained at greater than 5. Periodic reliming may be necessary to ensure that the chromium is immobilized in the soil.

Status of the Technology. Laboratory data support the theory of this treatment method. Soils have been treated under field conditions. The in situ reduction of hexavalent chromium to trivalent chromium has been accomplished in Arizona well water by using minute quantities of a reducing agent (Sanning and Black 1987).

In Japan, remedial action was taken at sites contaminated by the disposal of chromite roast residues from the manufacture of sodium bichromate. The primary contaminated areas were excavated, and secondary contaminated areas were treated with the reducing agent ferrous sulfate. The soluble hexavalent chromium was reduced to insoluble trivalent chromium (Sanning and Black 1987).

Secondary Impacts. Tillage increases the susceptibility of a site to water and wind erosion, and organic materials may have many effects on soil properties, including the following:

- Degree of structure.
- Water-holding capacity.
- Bulk density.
- Immobilization of nutrients, which hinders degradation of organic wastes.
- Reduction in soil erosion potential.
- Soil temperature.

Organic materials may also cause excessive nitrate levels in receiving waters, depending on the nitrogen content and degree of mineralization of the material.

Equipment, Exogenous Reagents, and Information Required. Power implements, tillers, applicators, and an irrigation system are necessary to apply reducing, acidifying, and liming materials. Run-on and runoff controls may have to be installed to prevent erosion and drainage problems. Reagents used include acidification agents (e.g., sulfur) and reducing agents (leaf litter, acid compost, or ferrous sulfate). Liming materials are also used. Additional information requirements prior to implementation are as follows:

- Characterization and concentration of metals, particularly Cr(VI), arsenic, mercury, and other constituents whose treatment requirements may be incompatible.
- Acidification, reduction, and liming reaction rates.

Advantages of the Addition of Reducing Agents to Treat Chromium. The advantages of this technique are as follows:

- Ease of application by standard agricultural methods.
- Has been demonstrated in the field.

Disadvantages of the Addition of Reducing Agents to Treat Chromium. This technique has the disadvantage that reliming may be necessary at intervals to ensure that the chromium is immobilized in the soil.

Addition of Reducing Agents to Treat Selenium

Hexavalent selenium [as selenate (SeO_4^{2-})], the dominant form of selenium in calcareous soils, is highly mobile in soils. Elemental selenium and selenite [Se(IV)] are less mobile in soils. Hexavalent selenium can be reduced to Se(IV) or Se under acid conditions. Reduction of selenium occurs naturally in soils. Elemental selenium is virtually immobile in soils. The Se(IV) will participate in sorption and precipitation reactions, but unlike the metals discussed previously, selenite is an anion (SeO_3^{2-}), and its potential leachability will increase with increasing pH. Therefore, at a site that contains selenium as well as other metals, selenium could not be treated if increased pH were required as part of the treatment for the other metals.

Selenium reduction studies have been limited to those involving the basic chemistry of selenium in soils. Wastes containing hexavalent selenium (SeO_4^{2-}) but no significant amounts of other metallic constituents are the most amenable to treatment by reduction. Before treatment, the soil must be acidified to pH 2 or 3 with sulfur or another agricultural acidifying agent. Acidification requirements for the particular soil must be determined experimentally. If site trafficability is suitable, leaf litter or compost are easily applied to soils by standard agricultural methods. Ferrous sulfate may be applied directly to the soil or through an irrigation system. Two moles of ferrous sulfate will reduce one mole of Se(IV). More than this amount should be added, however, to account for other reduction reactions that may occur in the soil. The quantity of organic material cannot be predicted from stoichiometric considerations.

The addition of reducing agents speeds up the natural process of selenium reduction in soils. Thus, the potential level of treatment should be high. Once reduction has occurred, however, the soil must be kept acidic. Reapplication of an acidifying agent may be necessary as required to maintain the pH at between 2 and 3.

Secondary Impacts. Low pH will adversely affect microbial activity and the degradation of organic waste constituents. Tillage may increase the susceptibility of the site to water and wind erosion. Organic materials may have many effects on soil properties, including:

- Degree of structure.
- Water-holding capacity.
- Bulk density.
- Immobilization of nutrients, which hinders degradation of organic wastes.
- Reduction of soil erosion potential.
- Soil temperature.

Organic matter may also result in excessive nitrate levels in receiving waters, depending on the nitrogen content and the degree of mineralization of the material.

Equipment, Exogenous Reagents, and Information Required. Power implements, tillers, and applicators are needed to prepare the site and to apply the acidifying agent and reducing agent. Runoff and run-on controls may be necessary to prevent erosion and drainage problems. Exogenous reagents required are sulfur or some other agricultural acidifying agent and ferrous sulfate. Additional information requirements prior to implementation of in-place treatment techniques for reduction of selenium are as follows:

- Characterization and concentration of metals, particularly selenium. (Treatment of selenium is incompatible with treatment of all other metals.)
- Oxidation state of metallic ions.
- Clay content of soil.
- Acidification and reduction reaction rates.

Advantages of Adding Reducing Agents to Treat Selenium. The advantages of this technique are as follows:

- Particularly amenable to the treatment of wastes containing hexavalent selenium but no significant amounts of other metals.
- Ease of application of reagents by standard agricultural methods.
- Potential level of treatment should be high.

Disadvantages of Adding Reducing Agents to Treat Selenium. The disadvantages of this technique are as follows:

- Not suitable for sites where an increased pH is required as part of the treatment for other metals.
- Acidification requirements must be determined experimentally.
- After reduction has occurred, soil must be kept acidic, which can entail reapplication of an acidfying agent.
- Organic matter can cause excessive nitrate levels in receiving waters.

3.3.1.3 Chemical Dechlorination Reactions

Chemical dechlorination processes use specially synthesized chemical reagents to destroy hazardous chlorinated molecules or to detoxify them to form other compounds that are considered less harmful and environmentally safer. In recent years, several dechlorination processes using different reagents have been developed to detoxify PCBs and many chlorinated organic compounds. The residue structures are generally nontoxic or lower in toxicity than the original compound. These processes were first developed for the treatment of PCB-containing oils, but several have potential application to in situ treatment of contaminated soils.

The reaction mechanism is nucleophilic substitution. Nucleophilic substitution removes chlorine from aromatic compounds by two mechanisms: the intermediate complex mechanism and the benzyne mechanism (Wilson 1987). Discussions of the dechlorination reactions in the following subsections are based on the reagent used in the process.

Acurex Process

The Acurex process is a two-step procedure. First, the organics are extracted from the soil with a special blend of solvents. The solvents are then treated with a proprietary sodium-based reagent to destroy the contaminants. In transformer oil, 2,3,7,8-TCDD has been reduced from 200 to 400 ppt to 40 ± 20 ppt by the Acurex process. The process has only been demonstrated to be applicable to treatment of PCB-contaminated oils. A commercial unit designed to treat soil is in the development stage (USEPA 1986). This process is not applicable to aqueous waste. The residues from the process include sodium chloride in sodium hydroxide solutions. It was noted that the sodium-based reagent process developed by Acurex Corporation should never be used in the field because of its explosive nature (Arienti et al. 1986).

PPM Process

The PPM process uses a proprietary sodium reagent to dechlorinate organic molecules. A solid polymer is generated (on the average about one 55-gallon barrel for every 10,500 gallons of oil treated). This substance (although regulated) can be more easily disposed of than the chlorinated organics. PPM currently has under development a dechlorination process designed to work on soils; however, no information is available on the process (Arienti et al. 1986).

Alkali Polyethylene Glycolate (APEG) Process

These processes use polyethylene glycols (PEG) or their derivatives that have been reacted with alkali (usually potassium) metals or their hydroxides to dechlorinate. When alkali metals are used, the reagents are susceptible to decomposition by water. The use of alkali metal hydroxides may solve this problem.

Dioxin and PCBs can be destroyed in soil by using reagents prepared from potassium and polyethylene glycols (KPEG). Moisture adversely affects the rate of the reaction. The APEG reaction with PCBs proceeds rapidly (from 10 minutes to several hours) under mild conditions in a nonpolar medium such as transformer oils or in hydrophobic solvent, such as toluene or hexane (Kornel and Rogers 1985).

In 1978, the Franklin Research Institute began studies to develop a dechlorination reagent. The research identified a compound that can be synthesized from sodium, polyethylene glycols, and oxygen. This reagent, called NaPEG, was formulated by mixing molten sodium (60 g) with 1 liter of polyethylene glycol having an average molecular weight of 400. It was first applied to the dechlorination of dielectric fluids containing PCBs. Later, this reagent (generally referred to as APEG) was also proven to be effective for the detoxification of dioxin-contaminated soils.

In the 1982 research performed by the U.S. EPA and Wright State University, actual dioxin-contaminated soils were effectively dechlorinated under laboratory conditions (Arienti et al. 1986).

Laboratory research conducted in 1985 by the U.S. EPA and Galson Research Corporation using 1,2,3,4-tetrachlorodibenzo-p-dioxin (TCDD) demonstrated that chlorinated dioxin levels in soil may be chemically reduced by applying APEG-type reagents (Arienti et al. 1986). In situ and slurry testing, with potassium hydroxide/polyethylene glycol 400/dimethyl sulfoxide (KOH/PEG/DMSO) and potassium hydroxide/2-(2-methoxy ethoxy ethanol)/dimethyl sulfoxide (KOH/MEE/DMSO) reagents on contaminated soils containing an initial concentration of 2000 ppb showed quite favorable results, which are presented in Tables 10 and 11. Several key factors were uncovered during these experiments:

- Temperature increases from 20° to 70°C during the in situ process indicated a dramatic improvement in reaction efficiency, i.e., an increase from 50 to 90 percent.
- No difference between reagent formulations was noted at 70°C during in situ testing.
- Dilution of the reagent with water was not effective in reducing the amount of reagent required during the in situ process.
- A removal efficiency of 99.5 percent TCDD (from 2000 ppb to 1 ppb) was realized after 12 hours at 70°C during the slurry processing.

Formulations of APEG containing polyethylene glycols having a molecular weight of 400 to 600 form biphasal systems with polar solvents and require agitation for intimate reagent-pollutant contact. In static systems, the reagent at the interphase is depleted, products will build up, and the reaction rates decrease. Although viscous reagents such as APEG-400 or 600 function quite well in biphasal agitated reactions, they are quite slow to penetrate and decontaminate soils that contain PCBs. Results of the study performed by EPA indicate promise for in situ application of the KPEG-350M reagent formulations (Kornel and Rogers 1985). A nonpolar solvent for PCB dissolution was used in the investigations of APEG-PCB reactions, and a reagent that is completely miscible with the hydrophobic and hydrophilic solvent was formulated. This reagent is based on polyethylene glycol monomethyl ether (average molecular weight of 350) and formulated with potassium hydroxide in either the pellet form or as a 60 percent solution. It is miscible with water as well as with hydrocarbons such as toluene, hexane, and other nonreactive solvents, and its viscosity is lower than the APEG 400 and 600 reagents. The characteristics of this reagent (called APEGM) indicate that it may be a useful candidate for in situ application.

Table 10. Summary of Results of In Situ Processing - All Soils Initially At 2000 ppb*

Reagent	Wt% in soil	Temperature, °C	Time, days	Final TCDD average concentration, ppb
1:1:1 KOH/PEG/DMSO	20	20	7	980
1:1:1 KOH/PEG/DMSO	20	70	7	<1
1:1:1 KOH/PEG/DMSO	20	70	1	5.3
2:2:2:1 KOH/MEE/DMSO/WATER	20	70	1	2.8
2:2:2:1 KOH/MEE/DMSO/WATER	20	70	1	3.3
2:2:2:1 KOH/MEE/DMSO/WATER	20	70	4	2.1
2:2:2:1 KOH/MEE/DMSO/WATER	20	70	7	1.2
2:2:2:6 KOH/MEE/DMSO/WATER	20	70	7	2.1
2:2:2:30 KOH/MEE/DMSO/WATER	50	70	7	18
2:2:2:30 KOH/MEE/DMSO/WATER	20	70	7	50
Blanks - All				<1

*Source: Peterson et al. 1985

Table 11. Results of Slurry Processing*

Reagent	Temperature, °C	Reaction time, h	Final TCDD concentration, ppb
1:1:1 KOH/PEG/DMSO	180-260	4	<1
1:1:1 KOH/PEG/DMSO	180	2	<1
1:1:1 KOH/PEG/DMSO	150	2	<1
1:1:1 KOH/PEG/DMSO	70	2	<1
1:1:1 KOH/PEG/DMSO	70	0.5	15
1:1:1 KOH/PEG/DMSO	25	2	36

Blanks - all <1 ppb TCDD

Spikes - % recovery in soil - 0.1-5.9

*Source: Peterson et al. 1985

This study investigated the effect of the APEG concentration and dilution in water and organic solvent on the dehalogenation of Aroclors 1242 and 1260 with potential application for the in situ destruction of PCBs in soil (Kornel and Rogers 1985). Polyethylene glycol monomethyl ether of average molecular weight [350 daltons (PEG-350M)], potassium hydroxide, toluene, and a proprietary solvent were used. The proprietary solvent was dimethyl sulfoxide (DMSO), patented by the Galson Research Corporation. It has been demonstrated that even dilution with H_2O to 50 percent by volume of the reagent can still yield an active dechlorination. The effect of increasing reactivity with increasing temperature was also demonstrated, which presents a viable input to the overall in situ application. Radio frequency ground heating (discussed in Section 3.4) can raise the surrounding strata to temperatures in excess of 400°C (Peterson et al. 1985). Therefore, it should be possible to heat soil to 60°C several feet deep over a selected area with minimal energy. Thus, a combination of the reagent, proprietary solvent, and radio frequency heating is promising for the in situ treatment of heavily contaminated soils.

Brunelle and Singleton (1985) reported that the more highly chlorinated PCB mixtures (e.g., Aroclor 1260, Aroclor 1254) react readily with PEG/KOH or PEGM/KOH at temperatures as low as -6°C, and contaminated soil samples may be effectively treated with this reagent.

In a two-step process reported by Novinson (1985) polychlorinated biphenyls are first reduced to unsubstituted biphenyl by using a mild reducing agent such as sodium borohydride in methanol/water. This is followed by oxidation with potassium permanganate to yield simpler, less-toxic, and more-biodegradable organic carboxylic acids. This process can be used on site to treat contaminated soils; however, no data are available.

Whereas laboratory studies investigated in situ applications of APEG to contaminated soils, recent research has focused on slurry application of the reagent to dioxin-contaminated soils and wastes. The APEG process has been tested in the laboratory on 2,3,7,8-TCDD-contaminated soils (USEPA 1986). In a laboratory-scale slurry process, PCDD- or PCB-contaminated soil (2000 ppm) was reacted with the KPEG reagent, and the concentration was reduced to below 1 ppb after being heated to 75°C and being mixed for 2 hours. The reagent was removed for reuse (>90 percent). A 1 to 10 ton/day slurry process is being prepared for field verification on actual waste.

The results obtained by using the IT/SEA Marconi reagent (a polyethylene glycol-based mixture) to treat a PCB-contaminated concrete floor indicate the reagent is effective in reducing the concentration of PCBs on the surface or contained within the upper 1/2 inch of concrete (Taylor et al. 1989).

Status of the Technology. Chemical dechlorination with different reagents has been tested both as a batch reactor process and an in situ process. To date, the batch reactor process has been more successful in terms of destruction efficiency. The estimated cost of the batch process is less because the chemical reagent can be recovered under enclosed and controlled conditions, whereas a chemical reagent that is added directly to the soil in the field cannot be recovered. In general, an in situ process is desirable when a large quantity of contaminated soil is involved in which the level of contamination is not extremely high (10 to100 ppb). In these cases, the quantity of soil that would have to be excavated to destroy a small quantity of contaminant may not be justified (Arienti et al. 1986).

Secondary Impacts. Heating the soil, which is necessary for the reaction to occur, may cause increased microbial activity in the area as well as changes in other soil properties. The application of reagent to the soil surface may cause the formation of reaction byproducts that are not well understood and may be more toxic than the contaminants being treated.

Equipment, Exogenous Reagents, and Information Required. Methods for heating the soil, delivering the reagent to the contaminated subsurface, and mixing the reagent and the soil are required. An alkali metal hydroxide (e.g., KOH) and polyethylene glycol (PEG) are the required reagents. A solvent and water may also be necessary depending on the specific reaction.

The following information is required before implementation of this technique:

- Vertical and areal extent of contamination.
- Soil physical characteristics (percentage clay, sand, etc.).
- Types of chemical contaminants.
- Soil moisture content.

Advantages of the APEG Process. The advantages of the APEG process for in situ treatment of soils are as follows:

- The process is effective for treating PCBs, TCDDs, and other chlorinated hydrocarbons.
- The reagents are readily available.

Disadvantages of the APEG Process. The disadvantages of the APEG process are as follows:

- Water can adversely affect the rate of reaction.
- Reaction byproducts are currently not well understood.
- The need to deliver, mix, and heat the reagent and the soil in situ may limit the applicability of the technology.

3.3.1.4 Polymerization

A polymer is a large molecule built up by the repetition of small, simple, chemical units. A polymerization reaction is the conversion of a particular compound to a larger chemical multiple of itself (Kirk Othmer 1982). The resulting polymer often has physical and chemical properties different from the initial unit, and it could be less mobile in the soil system.

Demonstration has shown that naturally occurring iron and sulfates in contaminated soil may catalyze initial polymerization of contaminants. Treatment solutions containing sulfate-related constituents have been used successfully in polymerization reactions in the soil (Williams 1982).

While working with grouting materials and polymeric agents, Mercer et al. (1970) found the process of in situ immobilization with these agents expensive and complicated by the logistics of obtaining widespread coverage without an excessive number of injection wells.

Chemical polymerization is most effective for immobilization of organic constituents, preferably those with more than one double bond. General categories of constituents suitable for polymerization include aliphatic, aromatic, and oxygenated monomers such as styrene, vinyl chloride, isoprene, acrylonitrile, etc. When used for multiorganic contamination, the catalysts and activators necessary to achieve polymerization may interact with one another.

A 2:1 ratio of the volume of catalyst and activator to the volume of contaminant is used. Two applications of the catalyst and activator are required, and they should be applied separately to prevent reactions before they contact with wastes. A wetting agent is added to promote rapid and uniform dispersion of solutions throughout the contaminated area. If ground temperature falls below 50°F, it may be necessary to warm the treatment solution to 50°F before its use. Because of the acidic nature of treatment reagents, corrosion-resistant application equipment is required.

If the surficial zone is too shallow to tolerate sufficient injection pressure for dispersing catalyst and activator solutions, installation of exfiltration galleries is required (e.g., a 2-inch-diameter perforated PVC casing, buried in trenches below ground surface across the contaminated zone). A riser pipe and manifold header connect each gallery to solution tanks containing the catalyst and the activator.

This technology is moderate to difficult to apply. In a field study, it was found that obtaining widespread coverage was difficult without an excessive number of injection wells.

The level of treatment achievable varies and depends on waste and soil conditions. The potential for long-term immobilization is unknown at this time.

The polymerized area may exhibit decreased infiltration and permeability. Catalysts and activators are needed. Vendors should be consulted as to equipment needs.

Boyd and Mortland (1985) describe the formation of dibenzo-p-dioxin radical cation and polymerization on a simple clay mineral [Cu(II)-smectite] under mild conditions. The radical cation polymerized to form dimers and trimers. Radical cations of 1- and 2-chlorodibenzo-p-dioxin were also formed on Cu(II)-smectite. The results of this work suggest the possibility for detoxification of dioxins through catalysis by a simple mineral material.

In situ polymerization was successfully performed to remedy a 4200-gallon acrylate monomer leak from a corroded underground pipeline into a glacial sand and gravel layer (Sanning and Black 1987). Soil borings indicated that as much as 90 percent of the monomer had been polymerized by injection of a catalyst, an activator, and a wetting agent.

Status of the Technology

The reliability of the treatment is unknown because no information exists regarding its long-term effectiveness. In situ polymerization is suitable mostly for ground-water cleanup after land spills or underground leaks of the pure monomer. Applications to uncontrolled hazardous waste sites are limited.

Secondary Impacts

The polymerized area may exhibit decreased infiltration and permeability.

Equipment, Exogenous Reagents, and Information Required

Corrosion-resistant application equipment is needed because of the acidic nature of the treatment reagents. In some cases, exfiltration galleries are also required. A riser pipe and manifold header connect each gallery to solution tanks containing the exogenous reagents (catalyst and activator) used. Wetting agents are also required.

The following information is needed before the implementation of polymerization techniques:

- Characterization and concentration of wastes, particularly organics, at the site.
- Potential for polymerization of waste constituents.
- Polymerization products.
- Depth, profile, and areal distribution of constituents.
- Iron and sulfate content in soil.
- Catalysts and activators present in soil.
- Trafficability of soil and site.

Advantages of Polymerization

Polymerization offers the following advantages:

- Effective for immobilization of aliphatic, aromatic, and oxygenated monomers (e.g., styrene, vinyl chloride, isoprene, acrylonitrile).
- May be suitable for detoxification of dioxins through catalysis by a simple mineral material.

Disadvantages of Polymerization

This technology has the following disadvantages:

- The treatment can be expensive and complicated by the logistics of obtaining widespread coverage without an excessive number of injection wells.
- Technology can be difficult to apply.
- The reliability and long-term effectiveness of this treatment are unknown.
- Limited application and difficulty of initiating sufficient contact between the catalyst and the dispersed monomer are major disadvantages.

3.3.2. Biological Degradation

Biodegradation is an important environmental process that causes the breakdown of organic compounds. The ultimate goal of biodegradation is to convert organic wastes into biomass and harmless byproducts of microbial metabolism such as CO_2, CH_4, and inorganic salts.

Microorganisms (principally bacteria, actinomycetes, and fungi) make up the most significant group of organisms involved in biodegradation, and soil environments contain a diverse microbial population. Two types of parameters influence the rate of biodegradation:

1) Those that determine the availability and concentration of the compound to be degraded or that affect the microbial population site and activity.

2) Those that control the reaction rate.

Some of the important parameters affecting biodegradation include pH, temperature, soil moisture content, soil oxygen content, and nutrient concentration (Bonazountas and Wagner 1981).

Table 12 lists rate constants of organic compounds in soil. Table 13 presents rates in anaerobic systems.

Table 12. Biodegradation Rate Constants For Organic Compounds In Soil*

Compound	Test Method Die-Away (day^{-1})	 $^{14}CO_2$ Evolution (day^{-1})
Aldrin, dieldrin	0.013	
Atrazine	0.019	0.0001
Bromacil	0.0077	0.0024
Carbaryl	0.037	0.0063
Carbofuran	0.047	0.0013
Dalapon	0.047	
DDT	0.00013	
Diazinon	0.023	0.022
Dicamba	0.022	0.0022
Fonofos	0.012	
Glyphosate	0.1	0.0086
Heptachlor	0.011	
Lindane	0.0026	
Linuron	0.0096	
Malathion	1.4	
Methyl parathion	0.16	
Paraquat	0.0016	
Parathion	0.029	
Phorate	0.0084	
Picloram	0.0073	0.0008
Simazine	0.014	
TCA	0.059	
Terbacil	0.015	0.0045
Trifluralin	0.008	0.0013
2,4-D	0.066	0.051
2,4,5-T	0.035	0.029

*Sources: Lyman et al. 1982; USEPA 1988; Dragun 1988.

Table 13. Biodegradation Rate Constants For Organic Compounds In Anaerobic Systems*

Compound	In Soil Die-Away (day^{-1})	 $^{14}CO_2$ Evolution (day^{-1})	In sludge (day^{-1})
Carbofuran	0.026		
DDT	0.0035		
Endrin	0.03		
Lindane		0.0046	
PCP		0.07	
Trifluralin	0.025		
Mirex			0.0192
Methoxyclor			9.6
2,3,5,6-Tetrachlorobenzene			12.72
Bifenox			6.27

*Source: Lyman et al. 1982.

Prior to the implementation of in situ treatment techniques for modifying the soil properties, the following information is required:

- Characterization and concentration of wastes, particularly organics at site.
- Microorganisms present at site.
- Biodegradability of waste constituents (half-life, rate constant).
- Biodegradation products (partially hazardous byproducts).
- Depth, profile, and areal distribution of constituents.
- Soil properties for biological activity (such as pH, oxygen content, moisture and nutrient contents, organic matter, temperature, etc.).
- Soil texture, water-holding capacity, degree of structure, erosion potential of the soil.
- Trafficability of soil and site.

Four approaches are used or evaluated for in situ biological treatment of hazardous waste materials in contaminated soils:

1) Enhancement of the biochemical mechanisms for detoxifying or decomposing the soil contaminants.
2) Augmentation with exogenous acclimated or specialized microorganisms (mutants).
3) Application of cell-free enzymes.
4) Vegetative uptake.

Although it cannot be considered an in situ treatment, soil extraction/excavation followed by onsite biological treatment is one of the technologies most frequently used in bioremediation of hazardous waste sites.

3.3.2.1. Enhancement of Biochemical Mechanisms

Microorganisms (principally bacteria, actinomycetes, and fungi) are important in decomposition or detoxification processes. Therefore, treatments applied to the soil to enhance biological processes must not alter the physical environment in such a way that it would severely restrict microbial growth or biochemical activity. Based on these restrictions, treatments that may enhance microbial activity (biochemical mechanisms) in hazardous-waste-contaminated soil are discussed in the following subsections.

Colloidal Gas Aphrons

The introduction of microscopic bubbles of gas (gas aphrons) into the soil can enhance aerobic biodegradation of dissolved and dispersed organic contaminants by delivering gases at greater than their solubility limits. In laboratory experiments, colloidal gas aphrons have been shown to increase the concentration of gases present within the soil matrix.

Microscopic dispersions of a gas in water are referred to as colloidal gas aphrons (CGAs), which typically exist as 25- to 50-µm gas bubbles with the characteristics of a free-floating soap bubble. In the microdispersion media, CGAs have a film-like surface of sufficient strength to prevent their coalescence, even when pressed together (Michaelsen et al. 1984). Because they do not coalesce, the microscopic bubbles have a very large surface area. One liter of CGA containing 60 percent gas as 24-µm-diameter bubbles represents a total bubble surface area of 150 m^2 (Michaelsen et al. 1984). Any water-soluble surfactant and a gas of limited solubility (e.g., oxygen, carbon dioxide, or nitrogen) can be used to generate CGAs.

Because they are so small, CGAs can remain in suspension and flow through channels such as those that exist in sandy soils. They may also be pumped with positive displacement pumps without losing their integrity or characteristics (Michaelsen et al. 1984).

Sebba and Barnett (1981) describe how CGAs are formed. A rapid stream of dilute surfactant solution is passed through a Venturi throat, where a restricted orifice is located. At this point, gas (usually air) is sucked into the stream under an excess pressure of about 1 atmosphere. As a result of the turbulent jet and the slow entry of the gas, the solution enters in the form of microbubbles. For a shell-encapsulated bubble to be generated, the gas must break through (at least twice) an aqueous-gas surface that has a surfactant monolayer at the surface. The turbulence ensures that, in contact, a '"bubble" introduced by sparging through a fitted disc or by gas precipitation is likely to be gas surrounded by the bulk water and have only one interface; therefore, it essentially is a gas-filled hole. A high concentration of CGA bubbles is obtained by recycling the suspended gas bubbles in solution through the CGA generator a few times.

In situ laboratory degradation studies (Michaelsen et al. 1984) have shown that injecting a combination of CGAs and *Pseudomonas putida* plus microbial nutrients into an anaerobic sand matrix spiked with 300 µg/L phenol degraded 60 percent of the phenol in 24 hours. The CGAs converted the anaerobic matrix into an aerobic environment, which allowed the *P. putida* to degrade the contaminant.

The use of CGAs at uncontrolled hazardous waste sites depends on the microdispersion as a source of oxygen for in situ bioreclamation. The contaminated medium retains the CGAs for much longer periods of time than it does air directly injected into the contaminated matrix because directly injected air moves rapidly toward the unsaturated zone and allows little oxygen retention.

This technology is applicable to waste sites contaminated with biodegradable chemicals. Potential treatment levels range from low to medium, depending on the waste types present. Treatment levels also depend on the soil type and condition and the accessibility of the contaminated area.

This technology may be applied with relative ease, depending on soil parameters. It is best suited for sandy soils.

Status of the Technology. Applications of colloidal gas aphrons have been limited to bench- and pilot-scale studies. This technology has not been demonstrated in field-scale studies.

Secondary Impacts. This technology increases soil oxygen levels dramatically , and the introduction of bacteria may cause other species present to decline in numbers. Also, certain wastes may be degraded into precursor species, which may or may not be less hazardous than the original contaminant(s).

Equipment, Exogenous Reagents, and Information Required. An injection plow is needed to inject CGAs into the soil matrix. The exogenous reagents needed include the CGA microdispersion, appropriate bacteriological species for the waste type to be decomposed, and nutrients to sustain the microbes during the decontamination process.

The following information is needed for effective application of this technology:

- Soil characteristics, e.g., particle size distribution and porosity.
- Bacterial species conducive to degrading waste(s) at the contaminated site.
- Area of contamination.

Advantages of CGA. The advantages of using this technology for hazardous waste site remediation are as follows:

- The cost of application is low.
- It enhances biodegradation of waste products.
- A wide variety of surfactants can be used to create the microdispersion.

Disadvantages of CGA. The disadvantages of this technology are as follows:

- Waste product can degrade into unknown compounds.
- Its application is limited because it is most appropriate for use in sandy soils.
- It does not completely degrade the waste products; wastes remain after the technology has been applied.
- Additional treatment is required for permanent remediation of a site.

Modification of Soil Properties to Optimize Environmental Conditions

Because the activity of microorganisms depends greatly on soil conditions, modification of soil properties such as moisture content, oxidation-reduction (redox) potential, pH, nutrient content, and temperature is a viable method for enhancing the microbial activity in the soil. Studies have shown that soil temperatures should be between 50° and 60°C (Atlas and Bartha 1981); soil potential should be greater than -15 bars (Sommers et al. 1981); pH should be between 5 and 9 (Alexander 1977, Atlas and Bartha 1981); and redox potential should be between pe + pH of 17.5 to 2.7 (Baas Becking et al. 1960). Soil pH and redox boundaries should be carefully monitored when chemical and biological treatments are combined. (Details of application methods for soil modification techniques are discussed in Appendix A.)

Soil Moisture. Moisture control may take the form of supplemental water to the site (irrigation), removal of excess water (drainage, wellpoints), a combination of techniques for greater moisture control, or other methods (e.g., soil additives). Furthermore, the addition of vegetation to a site will increase evapotranspiration of water and therefore assist in retarding the downward migration of water (i.e., leaching).

In a review of how soil water affects the decomposition processes in soils, including pesticide degradation, Sommers et al. (1981) suggested that, in pesticide degradation, the water alters general microbial activity and affects the kinds of microorganisms that are metabolically active in the soil. Ou et al. (1983) observed rapid mineralization of methyl parathion in soils at -0.1 and -0.33 bar soil moisture tension and the formation of bound residues. The ratio of the degradation products (p-nitrophenol to p-aminophenol) increased as the soils became drier. In dry soil (-15 bar), mineralization of methyl parathion and bound residue formation were slower. Limited experimentation indicates that degradation rates are highest at soil tensions between 0 and -1 bar.

The degradation of hazardous organic compounds can be accelerated by optimum soil moisture, and this approach may be sufficient to bring about the required degradation. For constituents relatively easy to degrade, however, more rapid treatment of the contaminated soil can be achieved when moisture control is used in combination with other techniques.

Various additives are available to enhance moisture control. For example, the water-retaining capacity of the soil can be enhanced by adding water-soluble substances. Nimah et al. (1983) evaluated three such synthetic substances for use in soils in arid areas and found that two of them increased the water content of the soil. Water-repelling agents that diminish water absorption by soils are also available. Conversely, water-repelling soils can be treated with surface-active wetting agents to improve water infiltration and percolation. Other soil characteristics that have been modified by surface-active agents include acceleration of soil drainage, modification of soil structure, dispersion of clays, and making soil more compactable. Evaporation retardants are also available to retain moisture in a soil.

Status of Technology. Moisture control practices are widely implemented in agriculture and are generally applicable to hazardous waste sites with certain precautions taken for leachate collection.

Secondary Impacts. Secondary impacts of some of these amendments or additives on soil biological activities, other soil physical properties, soil chemical properties, and environmental effects, (e.g., leachability and degradability) are discussed by Brandt (1972). Leaching of soluble hazardous compounds also may occur, especially when the soil-water partition coefficient is less than 10. Therefore, caution must be exercised at a hazardous waste site to ensure that drainage water disposed of offsite is not contaminated with hazardous substances. Provisions must be made to collect, store, treat, or recycle water that is not acceptable for offsite release. The drainage system should be managed to prevent or minimize contamination problems. Erosion may also be a problem.

Equipment, Exogenous Reagents, and Information Required. When natural precipitation is insufficient to maintain soil moisture within a near optimal range for microbial activity, irrigation may be necessary. Water can be applied by standard irrigation methods, i.e., subirrigation or overhead (sprinkler) irrigation. Irrigation should be applied frequently in relatively small amounts that do not exceed field capacity so as to minimize leaching (Fry and Grey 1971).

The ease of controlling moisture depends on how easily water is controlled at the site and on the availability of a suitable water source (e.g., transport distance, drilling of new wells, availability, and cost of energy for pumping). Controls for erosion and proper drainage to handle runoff are also necessary.

A properly designed drainage system either removes excess water or lowers the ground-water level to prevent waterlogging. Surface drainage is accomplished by a system of open ditches and buried tube drains into which water seeps by gravity. The collected water is conveyed to a suitable disposal point. Subsurface drainage may also be accomplished by pumping water from the wells to lower the water table. Like subsurface drains, wellpoints can be used to lower the table in shallow aquifers.

Information concerning the depth to the water table and the permeability of the soils is necessary. Vertical and horizontal hydraulic conductivities are also useful information.

Advantages of Moisture Control. Moisture control is a standard and relatively easy technique to implement. The required equipment and reagents are inexpensive and commonly available.

Disadvantages of Moisture Control. There is the possibility of generating drainage or leachate that is contaminated. Care must be taken to control drainage of this material.

Control of Oxygen for Aerobic Biodegradation. One reason for the common agricultural practices of tilling and draining the soil is to stimulate the decomposition of organic matter in an aerobic environment so that nutrients will be mineralized and made available for plant assimilation. Aerobic metabolism is more energy-efficient, and microbial decomposition processes are generally more rapid under aerobic conditions. Although the decomposition of some xenobiotic organic compounds appears to require anaerobic metabolism, most soil organisms shown to be active in the decomposition of pesticides and other xenobiotic compounds are aerobic (Alexander 1977; Pal et al. 1980, Baker and Mayfield 1980; Brunner and Focht 1983; Sims and Overcash 1981). Therefore, assuring the aerobiosis of the soil will often enhance the rate of biological decomposition.

Aerobiosis can also be maintained by the addition of air, oxygen, or other oxidants or oxygen sources (such as hydrogen peroxide, ozone, and nitrates). Gas injection or infiltration of water containing these alternative oxygen sources is being used for the reclamation of soil contaminated with hazardous wastes. Both ozone and hydrogen peroxide have been demonstrated to enhance dissolved oxygen levels in soil/ground-water systems and, consequently, to stimulate microbial activity. Ozone and hydrogen peroxide can also chemically degrade (oxidize) the contaminants completely or partially. Table 14 summarizes the advantages and disadvantages of some of these oxygen sources.

Yaniga and Smith (1986) observed an increase in the number of bacteria and in the degradation of gasoline with increasing oxygen concentration in soil columns treated with four different oxygen/air mixtures, a nitrogen and pure oxygen mixture, a pure oxygen, and a stabilized hydrogen peroxide solution.

Table 14. Oxygen Supply Alternatives*

Substance	Application method	Advantages	Disadvantages
Air	In-line	Economical	Not practical except for trace contamination <10 mg/L COD
	In situ wells	Constant supply of oxygen possible	Wells subject to blowout
Oxygen-enriched or pure oxygen	In-line	Provides considerably higher O_2 solubility than does aeration	Not practical except for low levels of contamination <25 mg/L COD
Hydrogen peroxide	In-line	Moderate cost Intimate mixing with ground water Greater oxygen concentrations can be supplied to the subsurface (100 mg/L H_2O_2 provides 50 mg/L O_2) Helps to keep well free of heavy biogrowth	H_2O_2 decomposes rapidly upon contact with soil, and oxygen may bubble out prematurely unless properly stabilized H_2O_2 is cytotoxic; however, organisms can be acclimated to high concentrations

*Source: Wagner and Kosin 1985

The applicability of microdispersion of air colloidal gas aphrons (CGAs) for treatment of liquid hazardous wastes by using 60 to 65 percent dispersion of air (or possibly oxygen, ozone, etc., as an oxygen source) has been tested in laboratory and in situ pilot studies. In situ biodegradation laboratory tests showed that the injection of a mixture of CGAs, *Pseudomonas putida*, and microbial nutrients into a saturated anaerobic sand matrix containing 300 mg/L of phenol solution resulted in 60 percent degradation of the phenol in 24 hours (Michelsen et al. 1984).

Tilling the soil for aeration, a common practice in agriculture, has been recommended for the reclamation of soil contaminated with hazardous wastes by practitioners and researchers (Arthur D. Little, Inc. 1976; Thibault and Elliott 1979). Rickabaugh (1988) reported that biodegradation of soil contaminants was favored by soil conditions similar to those obtained by tilling, i.e., mixing and aerobiosis followed by limited oxygen. Soils with high water tables that restrict aeration also may be drained by common agricultural techniques.

If the site is too wet, a drainage system must be installed. The soil can be tilled periodically to achieve aeration, and controls are necessary to prevent run-on and runoff of precipitation.

Achievable treatment levels range from low to high, depending on the biodegradability of the waste constituents and the suitability of the site and soil for maintenance of aerobic conditions. Retreatment at periodic intervals is necessary to assure that the soil oxygen is at a sufficiently high level.

Status of the Technology. The application of soil venting technology to increase aeration of subsurface soil has been investigated at field scale at the U.S. Air Force Engineering and Services Laboratory, Eglin AFB, Florida; by the Naval Civil Engineering Laboratory, Port Hueneme, California; and at Hill AFB, Ogden, Utah. Field-scale results obtained at Hill AFB indicated that soil venting stimulated biodegradation and that biodegradation may have resulted in 25 percent or more of the remedial action (Hinchee et al.1987).

Secondary Impacts. Tillage increases the susceptibility of the site to erosion. The use of oxidizing agents requires special treatment because they can react violently with certain compounds and can cause corrosion of the application equipment. They can also oxidize nontarget organic compounds and thus reduce the sorptive capacity of the soil being treated. Both hydrogen peroxide and ozone have two major limitations: they are toxic to bacteria and they may produce gas bubbles that block the pores in the soil matrix (Lee and Ward 1984). Hydrogen peroxide can also mobilize metals (Pb, An) (Wilson et al. 1986).

Equipment, Exogenous Reagents, and Information Required. A variety of equipment is available for aerating surface soils, all grouped under the category of tillers. Aeration of soils deeper than about 2 feet can be accomplished by air injection through wellpoints; however, aeration through wellpoints has been used and shown to be effective, primarily for saturated soils.

Hydrogen peroxide can be infiltrated through surface irrigation systems, shallow infiltration galleries, or ponds, or be injected into the subsurface through drains or injection wells, depending on the depth of the contaminated soil layers.

Advantages of Control of Oxygen for Aerobic Biodegradation. Oxidation can be achieved through the introduction of such additives as ozone and hydrogen peroxide as well as through tilling.

Disadvantages of Control of Oxygen for Aerobic Biodegradation. Delivery of the reagent to the subsurface is sometimes difficult. Extensive monitoring may be necessary to ensure uniform application of oxidizing agents.

Control by Oxygen for Anaerobic Biodegradation. There is increasing evidence that some halogenated xenobiotic compounds may be dehalogenated or completely degraded under anaerobic conditions (Suflita et al. 1982; Suflita and Tiedje 1983; Horowitz et al. 1983; Suflita et al. 1983; Kobayashi and Rittman 1982; Pfaender and Alexander 1972). Therefore, manipulation of contaminated soil to create an anaerobic reducing environment that enhances the decomposition of certain hazardous waste constituents should be considered. Apparently, the redox potential (Eh) of the environment must be below 0.35V for significant reductive dechlorination to take place, but exact requirements depend on the individual compounds being reduced (Kobayashi and Rittman 1982). Reductive reactions may be catalyzed by both abiotic and biochemical means in anaerobic environments.

When a recalcitrant compound has been altered by reductive reactions under anaerobic conditions, it may be more amenable to decomposition under aerobic conditions. For example, Munnecke et al. (1982) described the reductive dechlorination of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) under anaerobic conditions to 2,4-dichlorophenoxyacetic acid (2,4-D), which is readily degraded in the soil under aerobic conditions. Laboratory experimentation may show that anaerobic soil conditions followed by aeration enhances biological decomposition of some hazardous waste constituents; however, weekly alternations between anaerobic and aerobic conditions for enhancement of biodegradation of trichlorobenzenes in soil were evaluated, and no improvement in the mineralization rates was found (Marinucci and Bartha 1979). The trichlorobenzenes were mineralized most rapidly under continuous aerobic conditions. Other classes of compounds may not follow this pattern, however, and more research is needed for further evaluation of the potential for treatment by using alternating anaerobic and aerobic conditions. Longer periods between alternations may be appropriate.

Biodegradation can also be stimulated by adding other electron acceptors, such as nitrates. Microorganisms using nitrates as electron acceptors can degrade some phenols and cresols (Wilson et al. 1986) and some low molecular-weight polycyclic aromatic hydrocarbons (Luthy and Mihelcic 1987). Kuhn et al. (1985) also reported that microorganisms present in river alluvium were able to respire nitrate that was degrading xylene. Although methanes and carbon tetrachloride can be degraded by nitrate-respiring microorganisms, chloroform and stable chlorinated ethylenes or ethanes (i.e., in oxygenated water) cannot (Bouwer and McCarty 1985). Based on their studies, Major et al. (1988) concluded that the addition of nitrate to gasoline-contaminated ground water might be a more economical and effective remedial action than aeration. Battermann and Werner (1984) also used nitrate as an alternative oxygen source for decontamination of an oil spill in the upper Rhine catchment. By adding nitrate (50 lb) and nutrients to recovered ground water (in-line) and then injecting it back into the saturated zone, they were able to remove 16.6 tons of hydrocarbon retained in the pore volume of the formation in about 300 days. Laboratory column studies have shown that m-xylene is rapidly mineralized in the absence of molecular oxygen and with nitrate as electron acceptor (Zeyer et al. 1986). In general, the results from these anoxic column studies (e.g., ground-water infiltration zones, sludge digestors) seem to indicate that aromatic hydrocarbons may be mineralized in the absence of molecular oxygen. Suflita and Gibson (1984) reported reductive dehalogenation, but not degradation, of naturally occurring aromatics in environments where the levels of sulfate were relatively high and where sulfate respiration was taking place.

Arthur D. Little, Inc. (1976) reported that a proven method of creating anaerobic conditions is to dike and flood the soil in a fashion similar to that used to grow rice. They cite unpublished work by W. Farmer at the University of California at Riverside, in which a 1.5-acre DDT-contaminated field was amended with organic matter and flooded and the soil temperature was increased. The DDT was completely transformed into DDD in 18 days. They suggest that, without this treatment, the transformation to DDD would have taken more than 2 years. Because flooding the soil presents opportunities for leaching hazardous materials from contaminated soil, it is probably not advisable in most soils contaminated with hazardous wastes. It should be possible to lower the redox potential of the soil, however, by adding excessive amounts of readily biodegradable organic matter, compacting the soil to reduce oxygen diffusion through large soil pore spaces, keeping the soil wet without exceeding the gravitational water potential (field capacity), and perhaps deep mulching to impair oxygen diffusion to the soil surface.

Reductive dehalogenations or other reductive reactions that lead to decomposition or detoxification of specific hazardous waste constituents should be verified in the literature or through experimentation before this treatment is used.

Depending on the degradative pathway of the constituents, the treatment levels achieved may range from low to high. This technology may result in only partial degradation, and aerobic conditions may have to be established to complete the treatment. Retreatment may be required to maintain anaerobic conditions. This treatment may range from moderate to difficult to apply. Run-on and runoff controls are necessary.

Status of the Technology. Few applications of this method of inducing anaerobiosis, either in the field or under laboratory conditions, have been reported (McLean et al. 1988).

Secondary Impacts. Inducing anaerobic conditions may result in the formation of toxic volatile forms of metals (e.g., methylated mercury and arsines), hydrogen sulfide, and other nuisance odor compounds. Leaching of hazardous constituents may also occur if water addition is not carefully controlled. Organic materials may affect soil properties such as degree of structure, water-holding capacity, bulk density, and temperature. They can also immobilize nutrients, which hinders the degradation of organic wastes and reduces soil erosion potential. Organic materials can also cause excessive nitrate levels in receiving waters, depending on the nitrogen content and degree of mineralization of the material. In the field, the addition of organic materials to create anaerobic conditions is only conceptual.

Equipment and Exogenous Reagents Required. Power implements, compactors, and an irrigation system are necessary. The exogenous materials required are irrigation water and organic materials (e.g., mulches).

Irrigation water for inducing anaerobiosis can be applied by use of standard irrigation practices. Mulches also may be applied to act as a barrier to oxygen diffusion into the soil. Surface soil may be compacted to reduce porosity. Reducing pore size and restricting reaeration will increase the anaerobic microsite frequency in the soil. Compaction helps to draw moisture to the soil surface, which lessens the problems of leaching that can occur if anaerobiosis is achieved by water addition. If the compaction itself should prove inadequate to achieve the required degree of anaerobiosis, water could be added.

Because less water should be required in a compacted soil than in an uncompacted soil, the leaching potential would be minimized. Readily biodegradable organic materials are applied and incorporated into the soil so that the soil microbial population will rapidly deplete the oxygen and create anaerobic conditions while degrading these materials.

Advantages of Control of Oxygen for Anaerobic Biodegradation. Some recalcitrant aromatic hydrocarbons can be degraded under anaerobic conditions.

Disadvantages of Control of Oxygen for Anaerobic Biodegradation. Creating anaerobic conditions in the soil involves manipulating the soil in a complex manner (i.e., moisture control, organic amendment, compaction, and mulching). Flooding, one method of inducing anaerobiosis, presents opportunities for leaching hazardous materials from the soil.

Soil pH. Depending on the nature of the hazardous waste components contaminating the soil, it may be advantageous to optimize the soil pH for a particular segment of the microbial community because both structure and activity are affected by the soil pH (Gray 1978, Alexander 1977). Some fungi have a competitive advantage at slightly acidic pH, whereas actinomycetes flourish at slightly alkaline pH (Alexander 1977). Soil pH has also been shown to be an important factor in determining the effect various pesticides have on soil microorganisms (Anderson 1978). Near neutral pH values are probably most conducive to microbial functioning in general. The discovery that fungal metabolism of polynuclear aromatics hydrocarbons (PAHs) is qualitatively similar to mammalian metabolism in that mutagenic arene oxides (epoxides) are produced as initial oxidation products (Cerniglia and Gibson 1979, Cerniglia et al. 1979) suggests that fungal degradation of PAHs in the environment should be discouraged. Although the effect of soil pH on the formation of epoxides from PAHs has not been demonstrated, it may be advantageous to maintain the pH near 7 to encourage a relatively higher bacterial activity in soils contaminated with these compounds. Laboratory studies have shown that increasing soil pH values from acidic to neutral results in an increased biodegradation rate for benzo(a)pyrene and that mutagenic characteristics for metabolites 7,12-dimethylbenz(a)anthracene formed in acidic and neutral soil were similar (Park et al. 1988). Laboratory studies also have shown that soil pH values higher than those found at the Chem-Dyne Site enhanced the decomposition of some contaminants of interest (Rickabaugh 1988). This investigation also demonstrated that although adjusting the soil moisture content to 20 percent and the pH to about 8 resulted in a greater decline of chlorinated hydrocarbons (compared with the controls), maintaining this high pH appeared to retard this decline (Rickabaugh 1988).

In agriculture, the application of fluid lime is becoming more popular, especially when it is mixed with fluid nitrogen fertilizer. The combination results in fewer trips across the soil, and the lime counteracts the acidity produced by the nitrogen. Limestone has also been applied successfully through a spray irrigation system to a land treatment facility where pharmaceutical wastewaters are treated. Thus, this technique would be suitable at hazardous waste sites. Contaminated soil may have to be treated with crushed limestone or lime products to raise the pH to the desired range, or with acid-producing materials or sulfur to lower the pH.

Lime treatment for soil pH adjustment is dependent on several soil factors, including soil texture, type of clay, organic matter content, and exchangeable aluminum (Follett et al. 1981). The buffering capacity of the soil reflects the ability of the soil components to hold a large number of ions in adsorbed or reserve form. Thus, adsorption or inactivation of H^+ ions or the release of adsorbed ions to neutralize OH-ions provides protection against abrupt changes in pH when acidic or basic constituents are added to the soil. The varying buffering capacity among soils reflects differences in the soil cation exchange capacities and will directly affect the amount of lime required to adjust soil pH. The amount of lime required is also a function of the depth of contamination at the site (i.e., the volume of soil to be treated). Because no guidelines for adjusting soil pH are readily available, the amount of lime required to effect a pH change in a particular site/soil/waste system must be determined by a soil-testing laboratory in short-term treatability studies or soil-buffer tests (McLean 1982).

The achievable level of treatment is high, depending on the biodegradability of the wastes and the suitability of the site and the soil. Lime and acidification requirements for a particular soil have to be determined experimentally. The buffering capacity of the waste also must be considered. Thorough mixing is required in the zone of contamination to effect pH change. Because the soil is tilled, runoff and minor controls are necessary to control drainages and erosion. This technology ranges from easy to difficult to apply, depending on the trafficability of the soil and the depth of contamination. Reliming or reacidification is necessary as treatment progresses.

Status of the Technology. Soil pH control is commonly practiced in agriculture and in pollution control processes to neutralize toxic substances. In agriculture, acidification is practiced much less commonly than liming. Adjustment of pH is often reported in laboratory tests, but less information is available on the application of this technique in pilot-scale studies or in the field.

Secondary Impacts. Changes in soil pH affect dissolution or precipitation of materials within the soil. Care must be taken to assure that raising or lowering of soil pH does not increase the mobility of hazardous materials. Tillage increases the susceptibility of the site to erosion.

Equipment and Exogenous Reagents Required. Applicators, tillers, and power implements are required. Depending on the wastes and the soil characteristics, liming or acidifying material is required.

Advantages of Soil pH Control. The technology is widely practiced with positive results. The required additives are readily available.

Disadvantages of Soil pH Control. Because thorough mixing is required, extensive disturbance of contaminated soils may occur. Proper personnel health and safety protections must be implemented.

Soil Nutrients. As in the case of all living organisms, microorganisms must have specific inorganic nutrients (e.g., nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, iron, and trace metals) and a carbon and energy source to survive. The organic contaminants present in the soil may provide the carbon and energy source and serve as primary substrates. If the compound of interest is only degraded cometabolically, however, a primary substrate must be made available for the microbial population. The primary source of carbon may already be present in the soil or it may be added (e.g., glucose, acetate, citrate). Carbon sources also could be added if the concentration of contaminants present in the soil are not sufficient to support an active microbial population; however, the addition of these compounds could inhibit the biodegradation of the compound(s) of interest as a result of preferential degradation. Laboratory anaerobic studies performed with 4-nitrophenol-contaminated topsoil have shown that adding glucose (50 mg/kg) reduced the half-life of the 4-nitrophenol from 12 to 6 days (Lokke 1985).

Although most microorganisms can efficiently extract inorganic nutrients from their environment, their activity may be limited by the availability of nutrients. This is especially true if available carbon is excessive relative to the amount of nitrogen or phosphorus the microorganisms need to degrade it. If the soil organic carbon, organic nitrogen, and organic phosphorus are determined, the C:N:P ratio can be determined and nutrient availability can be evaluated. If the ratio of organic C:N:P is wider than about 300:15:1 and available (extractable) inorganic forms of N and P do not narrow the ratio to within these limits, supplemental nitrogen or phosphorus should be added (Alexander 1977, Kowalenko 1978). Lokke (1985) reported that adding 50 mg/kg of nitrate-N under anaerobic conditions to soil concentrated with 4-nitrophenol could reduce the half-life of this compound from 12 to 10 days. Thorton-Manning et al. (1987) found that whereas the addition of nitrate and phosphate resulted in faster and more extensive mineralization of phenol in subsurface horizons, it did not stimulate degradation in the upper horizons of contaminated soil. Excesses or deficits of nitrogen or phosphorus brought about by the addition of any organic amendments should be taken into account, and commercial fertilizers can be used to make up any deficit.

In agriculture, fertilizer is added to hasten the decomposition of crop residues (Alexander 1977); this procedure also has been used in the treatment of soil contaminated with hazardous wastes as a result of an oil spill (Thibault and Elliott 1980). Skujins et al. (1983) studied the biodegradation of waste oils at a disposal site where soils were amended with calcium hydroxide, phosphate, and urea. Within 4 years, 90 percent of the applied oil was degraded.

Standard agricultural methods are used to add fertilizers to the soil. Depending on the nutrient type, physical state, solubility of the fertilizer, and depth of contamination, the fertilizer is incorporated into the soil as necessary. Power implements, tillers, and applicators are required to apply the fertilizer to the soil. If nutrient availability is limiting or retarding microbial degradation or detoxification of organic hazardous waste constituents, the achievable level of treatment could be increased by making the nutritional characteristics of the site and soil more suitable.

Sufficient nitrogen and phosphorus must be reapplied to ensure that these nutrients do not limit the microbial and metabolic activity. Controls to manage the run-on and runoff at the site are necessary to prevent drainage and erosion problems. This technology ranges from easy to difficult to apply, depending on the trafficability of the site.

Status of the Technology. Commonly used in agriculture, this technology has been used in the bioremediation of contaminated ground water and in the treatment of oil wastes. Commercially available nutrient solutions are especially formulated to prevent precipitation of the chemical nutrients.

Secondary Impacts. Nitrogen must be applied to the soil cautiously to avoid excessive nitrate formation. Nitrate or other forms of nitrogen in the soil that oxidize to nitrate may be leached to ground water. Also, some nitrogen fertilizers tend to lower the soil pH, which necessitates a liming program to maintain an optimum pH for biological activity. Tillage will increase the susceptibility of the site to erosion.

Equipment and Exogenous Reagents Required. Power implements, tillers, and applicators are required to apply the fertilizer containing inorganic nutrients (nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, iron, and trace metals) to the soil. Carbon in the form of glucose, acetate, citrate, etc., also may have to be added. Lime may also be required.

Advantages of Soil Nutrient Addition. This technique is extremely effective in enhancing microbial activity resulting decomposition of organic contaminants. Equipment and additives are readily available.

Disadvantages of Soil Nutrient Addition. Retreatment may be necessary at intervals as nutrients are used up in the process. Also, liming and reliming may be necessary to maintain optimal pH for biological activity.

Soil Temperature. Soil temperature is one of the most important factors controlling microbiological activity and the rate of decomposition of organic matter. It also influences the rate of volatilization of compounds from soil. Soil temperature can be modified by regulating the oncoming and outgoing radiation or by changing the thermal properties of the soil (Baver et al. 1972). Laboratory studies have shown that the rate and extent of low-molecular-weight PAHs removed from agricultural soils can be significantly enhanced by increasing the soil temperature. Conversely, temperature had little effect on the removal of five- and six-ring PAHs (Coover and Sims 1987a).

Thorton-Manning et al. (1987) evaluated the importance of soil temperature and inorganic nutrient availability in the stimulation of phenol biodegradation in surface and subsurface soils. These researchers found that, the effect of temperature on mineralization was a function of the soil type. They also found that, whereas the addition of nitrate and phosphate resulted in faster and more extensive mineralization of phenol in the subsurface horizons, it did not stimulate degradation in the upper horizons. Bachmann et al. (1988) reported that temperatures in the 20° to 30°C range were the most favorable for biological degradation of alpha-hexachlorocyclohexane (HCH) in contaminated soil. At temperatures below 4°C and above 40°C, they were unable to detect biological degradation of alpha-HCH.

Because of the insulating properties of plant cover, vegetation plays a significant role in soil temperature. Bare soil unprotected from the sun's direct rays becomes very warm during the hottest part of the day; it also loses its heat rapidly during colder seasons. A well-vegetated soil, however, does not become as warm as a bare soil during the summer, and the vegetation acts as an insulator to reduce heat loss from the soil in the winter. Frost penetrates more rapidly and deeper in bare soils than in soils under a vegetative cover.

Mulches can affect soil temperature in several ways. Mulches generally reduce diurnal and seasonal fluctuations in soil temperature. In the middle of the summer, mulched and bare plots differ very little; however, mulched soil is cooler in the winter and fall and warms up more slowly in the spring. Because mulches with low thermal conductivities decrease heat flow both into and out of the soil, soil will be cooler during the day and warmer during the night. White paper, plastic, or other types of white mulch increase the reflection of incoming radiation, which reduces excessive heating during the day. A transparent plastic mulch transmits solar energy to the soil and produces a greenhouse effect. A black paper or plastic mulch absorbs radiant energy during the day and reduces heat loss.

Irrigation increases the heat capacity of the soil, raises the humidity of the air, lowers air temperature over the soil, and increases thermal conductivity; the result is a reduction of daily soil temperature variations (Baver et al. 1972). Sprinkle irrigation, for example, has been used for temperature control (specifically, frost protection in the winter and cooling in the summer) and for the reduction of wind erosion of the soil (Schwab et al. 1981). Drainage decreases the heat capacity and thereby raises the soil temperature. Elimination of excess water in the spring results in a more rapid temperature rise. The addition of humic substances improves soil structure, which improves soil drainability and results indirectly in higher soil temperature.

Several physical characteristics of the soil surface can be modified to alter soil temperature (Baver et al. 1972). Compaction of the soil surface increases the density and thus the thermal conductivity. Tillage, on the other hand, creates a surface mulch that reduces the heat flow from the surface to the subsurface. The diurnal temperature variation in a cultivated soil is much greater than that in an untilled soil. A loosened soil is cooler at night and more susceptible to frost.

Mulches not only modify the soil temperature, they also protect the soil surfaces from erosion and reduce water and sediment runoff. Because this prevents surface compaction or crushing and conserves moisture, the achievable level of treatment could be high when site and soil characteristics are suitable.

Status of the Technology. Application of mulches to soil to increase soil temperature is commonly used in agriculture. No laboratory or field studies, however, have been reported in which this technique has been used in the treatment of soils contaminated with hazardous wastes. Nevertheless, application of mulches may be useful for controlling soil temperature at contaminated sites. Also, the techniques used to modify soil characteristics (irrigation, tillage, etc.) indirectly modify the soil temperature.

Secondary Impacts. Few secondary impacts have been identified for this technique.

Equipment and Exogenous Reagents Required. The type of mulch required determines the application method. Commercial machines are available for spraying mulches. Hydromulching is a process in which seed, fertilizer, and mulch are applied as a slurry. Plastic mulches are applied mechanically with equipment that is towed behind a tractor; the plastic strips are sealed at the edges with soil. For treatment of large areas, special machines are available that glue polyethylene strips together (Mulder 1979). If irrigation or drainage is used to modify the heat capacity of the soil, appropriate irrigation/drainage systems are needed. Power implements, tillers, and applicators are usually required to apply this technique.

Advantages of Soil Temperature Control. Optimal soil temperature greatly enhances biodegradation and affects volatilization of organics.

Disadvantages of Soil Temperature Control. The techniques of temperature control commonly practiced do not allow for minute changes in temperature.

Addition of Nonspecific Organic Amendments

Stimulating general soil microbial activity and population size through the addition of organic matter increases the opportunity to select organisms that can degrade hazardous waste components. High microbial activity allows cometabolic processes to act on recalcitrant hazardous waste components. The addition of manures, plant materials, or wastewater treatment digestor sludge at levels characteristic of composting may prove valuable to biological treatment of soil contaminated with hazardous wastes (Kaplan and Kaplan 1982a, Doyle and Isbister 1982).

Extensive laboratory research has shown that supplemental carbon and energy sources can stimulate the metabolism of xenobiotic, often recalcitrant compounds. The breakdown or transformation of these compounds can be through cometabolism (Alexander 1981; Keck et al. 1989; Sims 1986), or metabolism of the compound may simply be stimulated by the supplemental carbon and energy source (Yagi and Sudo 1980). Bachmann et al. (1988), however, reported that adding an auxiliary carbon source (variable acetate/glucose mixtures) showed inhibitory effects on alpha-hexachlorocyclohexane biomineralization in contaminated soils. Coover and Sims (1987b) indicated that manure addition had no apparent effect on the rate of disappearance of benzo(a) pyrene in soil. Based on the results of their laboratory studies, Schmidt and Alexander (1985) concluded that second substrate and uncharacterized dissolved organic carbon might play an important role in controlling not only the rate, but also the extent, of microbial degradation of organic contaminants present at low concentrations.

Composting of contaminated soil has been shown to degrade hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), whereas the ring structure of 2,4,6-trinitrotoluene (TNT) was not mineralized. The TNT residues were apparently strongly sorbed to the compost (Doyle and Isbister 1982). Camoni et al. (1982) demonstrated that adding organic compost to soil had no significant effect on the half-life (1 year) of 2,3,7,8-TCDD in soil. The degradation of pentachlorophenol and pentachloronitrobenzene in a laboratory composting system has also been studied (Sikora et al. 1982). Laboratory studies (Wilson 1987) have shown that aerobic composting of PCB-contaminated soils resulted in greater PCB removal than did anaerobic composting; the concentration decreased an average of 60 percent in 4 weeks. Several problems encountered during these studies and the fact that it is impossible to control weather conditions in a field situation have led to the conclusion that composting of PCB-contaminated soils is an uncertain technology.

Laboratory experimentation may be needed to determine the biochemical fate of given hazardous compounds in organically enriched soil or compost and to evaluate the environmental hazards associated with any residues and byproducts (Kaplan and Kaplan 1982b, Isbister et al. 1984). Residues may be more or less toxic than the parent compounds. Residues of hazardous compounds may not be extractable from organically enriched soil by use of ordinary solvents, which suggests the existence of a strong binding to organic matter or other soil constituents (Doyle and Isbister 1982, Khan 1982, Wallnofer et al. 1981, Bartha 1980, Stevenson 1972). Enzymatic activities of soil microorganisms can be responsible for coupling xenobiotic compounds and their breakdown products to soil humic materials (Bollag 1983, Bollag et al. 1983, Sjobland and Bollag 1981, Liu et al. 1981, Suflita and Bollag 1980, Bollag et al. 1980, Bollag et al. 1978). Careful monitoring for bound hazardous organic compounds, including toxic metabolites of hazardous parent compounds, should be performed. Humus-bound xenobiotic compounds may be slow to mineralize or be transformed to innocuous forms (Khan 1982, Chowdhury et al. 1981). In such cases, increasing the humic content of the soil may not be the method of choice.

Because pesticides and other residues have been shown to form stable chemical linkages with humic material in the process of humification, the incorporation of hazardous chemicals into soil humic material could represent a method for decontamination of soil. The binding and detoxification of hazardous chemicals are discussed by Bollag (1989).

Microbial decomposition of humic matter that contains bound hazardous organic compounds can release these compounds to the soil solution, where they are subject to leaching, volatilization, or reattachment to soil organic matter. This potential mobility of bound hazardous compounds suggests that treatment is not complete until their absence or safe level in the soil can be demonstrated (Bartha 1980, Saxena and Bartha 1983, Khan and Iverson 1982).

No examples of field trials of this treatment technique are available. Doyle and Isbister (1982) observed 55 percent degradation in 6 weeks of RDX in compost incubated in a greenhouse. In the same study, TNT levels were reduced by more than 99 percent within 3 weeks, but very little decomposition (mineralization) was observed. Field pilot-scale studies conducted at the Skrydstrup Chemical Waste Disposal Site (Denmark) are discussed in Section 3.3.2.5.

With the consumption of O_2, aerobic heterotropic bacteria oxidize arsenite (As^{+3}) to arsenate (As^{+5}). An available reserve of organic matter must be present in the soil for the oxidation to occur. Therefore, when arsenite contaminates a soil in concentrations that are below toxic levels for soil heterotrophs, the arsenite can be oxidized to arsenate by amending the soil with readily available organic matter and maintaining aerobic conditions in the soil. Quastel and Scholefield (1953) described the oxidation of arsenite in laboratory soil perfusion systems. Alexander (1977) and Konetzka (1977) have reviewed the microbial biochemistry of arsenic. Further treatment with ferrous sulfate will form highly insoluble $FeASO_4$. Biodegradable organic compounds as well as arsenite wastes are amenable to this treatment.

The potential achievable level of treatment ranges from low to high, depending on the solubility, sorption, and biodegradability of the organic constituents in the waste. Some arsenite may be bound to the soil and will not be available for oxidation. Available (extractable) arsenite should be quickly and completely oxidized. Hazardous constituents may initially be bound to organic materials, but they may later be released as organic materials decompose.

The quantity of organic material required must be determined in treatability studies. Nonspecific, readily biodegradable, organic matter should be present, and frequent mixing is required to maintain aerobic conditions. Run-on and runoff controls are required. This technology can be easy or difficult, depending on the trafficability of the soil and site and the depth of contamination. This technology may require reapplications for complete treatment.

Under anaerobic conditions, the added organic matter may result in the reduction and methylation of arsenic to volatile forms. Although anaerobic conditions must be avoided, anaerobic microsites are known to exist even in well-aerated soil, and some volatile metal compounds may be produced even in carefully managed soils.

Status of the Technology. Although extensive laboratory research has shown that supplemental carbon and energy sources can stimulate the metabolism of even recalcitrant compounds, no field trials have been run. Experimental soil systems have demonstrated the microbial oxidation of arsenite to arsenate, however.

Secondary Impacts. Organic materials may affect several of the soil properties (degree of structure, water-holding capacity, bulk density, etc.). Organic materials may also result in excessive nitrate levels in receiving waters, depending on the nitrogen content and degree of mineralization of the material. Tillage may increase the susceptibility of the site to erosion.

Equipment and Exogenous Reagents Required. Power implements, tillers, applicators, and proper drainage systems are required. The exogenous reagent required is organic material.

Cometabolism

Thomas and Ward (1989) define cometabolism as the biodegradation of an organic substance by a microbe that cannot use the compound for growth and hence must rely on other compounds for carbon and energy. Three mechanisms of cometabolism are discussed in the subsections that follow: 1) analogue enrichment; 2) nonanalogue enrichment with methane; and 3) other nonanalogue hydrocarbon substrates.

Analogue Enrichment. Adding a chemical analogue of a hazardous compound to a contaminated soil or to culture media can accomplish cometabolism of the hazardous compound (Keck et al. 1989; Sims and Overcash 1981; Pal et al. 1980; Furukawa 1982; Focht and Alexander 1970). Apparently, enzymes proliferated by microorganisms to metabolize an energy-yielding substrate structurally similar to a recalcitrant xenobiotic compound can sometimes transform the recalcitrant molecule cometabolically (Alexander 1981). For compounds in which the transformation product of the cometabolic process is not hazardous or is degradable by other organisms in the soil microbial community, analogue enrichment may be an effective treatment for contaminated soil. Sims and Overcash (1981) used analogue enrichment with phenanthrene to increase the rate of degradation of benzo(a)pyrene, which decreased the half-life by 35 percent. Biphenyl has been used to stimulate cometabolic degradation of PCBs (Furukawa 1982). Wilson and Wilson (1985) reported that exposing unsaturated soil columns to a mixture of air and natural gas for 3 weeks can stimulate trichloroethylene (TCE) biodegradation. Ninety percent of the applied TCE was mineralized (confirmed by the recovery of ^{14}C label). Whereas acclimation of sandy soil to an air/natural gas mixture has been shown to stimulate mineralization of chloroform, the addition of acetylene and methane inhibited chloroform oxidation (Strand and Shippert 1987).

Because chemical analogues to hazardous compounds or their degradation products may be hazardous, care must be taken in the selection and use of analogues for treatment.

Organic waste containing constituent(s) with analogues that have high rates of degradation by organisms without producing toxic products are amenable to treatment. The level of treatment may range from low to high, depending on the susceptibility of the hazardous constituent to cometabolism.

Analogue compounds are added in amounts large enough to stimulate microbial activity, but not large enough to be toxic to microbial functions or to have an adverse effect on public health and the environment. Treatability studies are needed to determine the feasibility, loading rate, and effectiveness of the analogue(s). The analogues may be applied as solids, liquids, or slurries and mixed thoroughly with the contaminated soil. Fertilization may be necessary to maintain microbial activity. Controls may be required to prevent drainage and erosion problems. Tillage will increase the susceptibility of the site to erosion.

No information is available on field application. Laboratory studies have shown that analogue enrichment can accomplish cometabolism. The reliability of this technology is unknown.

Nonanalogue Enrichment With Methane. Chlorinated alphatic solvents such as 1,1,1-trichloroethane and trichloroethylene, which are common contaminants of aerobic aquifers, appear to be biologically recalcitrant in the presence of oxygen; however, cometabolism of these compounds has been observed in environmental samples through enrichment with natural gas or methane and air (Thomas and Ward 1989). Methanotrophs, or methane-utilizing microorganisms, are selected as the microbial population when methane and air are introduced in soil samples. Colby et al. (1977) found that *Methyloccus capsulatus* produces a soluble, nonspecific monooxygenese that oxidizes methane as well as several alkanes, alkenes, and halogenated methanes. Several investigators have noted the cometabolism of such compounds as tetrachloroethylene, trichloroethylene, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1-dichloroethane, 1,2-dichloroethane, cis- and trans-1,2-dichloroethylene, 1,1-dichloroethylene, vinyl chloride, dichloromethane, carbon tetrachloride, and chloroform (Wilson and Wilson 1985; Fogel et al. 1986; Strand and Shippert 1986; Little et al. 1988). Fogel et al. (1986) found that the more heavily chlorinated compounds are degraded more slowly than the less chlorinated analogues and sometimes not at all.

Other Nonanalogue Hydrocarbon Substrates. Specific and nonspecific hydrocarbon substrates can be used to enhance cometabolism and specifically cooxidation (Keck et al. 1989). A soil isolate, *Nocardia* Strain 107-332, was found to cooxidize alkyl-substituted aromatic hydrocarbons to the corresponding acid while growing on n-hexadecane with no ring cleavage (Davis and Raymond 1961). Cooxidation studies by Raymond et al. (1967) identified several *Nocardia* species capable of aromatic ring dihydroxylation but not ring cleavage.

An increase in microbial numbers and the induction of the production of extracellular oxygenase may result in cooxidation of recalcitrant compounds in soil following the addition of nonspecific hydrocarbons (Keck et al. 1989). Bossert and Bartha (1984) noted that the addition of hydrocarbon substrates, such as oil to soil, can result in an overall increase in microbial activity if other nutrients are not limiting.

3.3.2.2. Augmentation With Acclimated or Mutant Microorganisms

Biological treatment methods described thus far have relied on the stimulation of microbial activity in the soil or on the natural selection of populations of microorganisms capable of degrading toxic waste constituents. Although these approaches show considerable promise for treating many kinds of organic hazardous waste constituents, the metabolic range of the natural soil microbiota may not be capable of degrading certain compounds or classes of compounds. Also, microbial metabolic specialists may not develop large enough populations under limited substrate conditions to degrade xenobiotic compounds rapidly enough to meet treatment criteria. In situations such as these, it may be advisable to add exogenously grown microorganisms to the soil. These microorganisms can be selected by enrichment culturing or genetic manipulation, and they can be acclimated to the degradation of different organic contaminants by repeatedly exposing them to the compound of interest. Microbial inoculants with a broad range of metabolic capabilities are available commercially, and experience with their use in both soil and aquatic systems contaminated with waste chemicals is expanding (Thibault and Elliot 1979, 1980; Walton and Dobbs 1980). Table 15 lists suppliers of biological products that have been or may be used to treat soils contaminated with hazardous wastes. Frequently, the application of microbial amendments to the soil is combined with other treatment techniques such as soil moisture management, aeration, and fertilizer addition.

Laboratory trials have demonstrated the potential of exogenously grown bacteria to degrade xenobiotic compounds quickly. Edgehill and Finn (1983) inoculated soil with *Arthrobacter* for the degradation of pentachlorophenol (PCP) and observed rapid degradation ($t_{1/2}$ <1 day) when the soil was incubated at 30°C. In soil treated under a roof where temperatures ranged from 8° to 16°C, PCP degradation was much slower, but it was much faster in mixed inoculated soil than in the control soil. Focht and Shelton (1987) found that although 3-chlorobenzoate was not degraded by the soil-indigenous microflora, it was completely metabolized in the presence of relatively small amounts of inoculum of *Pseudomonas alcaligenes* C-0 (102 cells/g).

Laboratory tests have shown that inoculation of soil columns with native microbial culture along with recycled effluent resulted in higher removals of chlorinated hydrocarbons than did inoculation with commercially available cultures (Sybron and Hydrobac) acclimated to these compounds (Rickabaugh 1988).

Chakrabarty (1987) used repeated applications of a "genetically engineered" *Pseudomonas cepacia* with the ability to mineralize 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and obtained 90 percent to essentially complete removal of 2,4,5-T from contaminated soil within 6 weeks. When the 2,4,5-T was exhausted, the population of *P. cepacia* became undetectable.

Thirty-four bacterial and five fungal PCB degraders have been discovered; however, none of the species could individually metabolize PCB and PCB isomers. Therefore, it may be necessary to use a consortium of more than two bacterial or fungal strains or a mixture of them to mineralize PCB and its isomers effectively (Wilson 1987).

Research involving white rot fungus (*Phanerochaete chrysosporium*) performed in recent years has demonstrated the ability of this fungus to degrade halogenated organic compounds, especially to dehalogenate and degrade chlorobenzene derivatives and to cleave aromatic rings (des Rosiers 1987). Laboratory studies of pentachlorophenol and related polyaromatic hydrocarbons seem to indicate that *P. chrysosporium* shows promise for in situ treatment of soils contaminated by wood-preserving materials. Field tests are planned for this year (Glaser et al.1989).

Table 15. Commercial Microbial Augmentation Products or Processes Used to Treat Hazardous-Waste-Contaminated Soils*

Vendor	Address	Product name(s)	Product description	Treatment
Flow Laboratories Environmental Cultures Division	Ingelwood, CA	DBC Plus; Types A, A-2,B,F and H-1	Formulated from specifically cultured bacteria preserved by freeze drying and air drying techniques.	25 lb/acre
General Environmental Science	Beachwood, OH	LLMO	Mixture of seven bacterial strains (*Bacillus, Pseudomonas, Nitrosomonas, Nitrobacter, Cellulomonas, Acrobacter, Rhodopseudomonas*) in liquid suspension.	(Site dependent)
Groundwater Decontamination Systems, Inc.	Waldwick, NJ	GDS process	Technique involves circulating water from the soil into an environmentally controlled tank. Nutrients are added, and the water is aerated. Treated water is returned to the soil. Air may be injected into the soil to stimulate further biodegradation.	(Site dependent)
Polybac/Cytox Corporation	Allentown, PA; San Francisco, CA; Gonzales, FL	Polysoil process	Mutant bacterial formulation, nitrogen and phosphorus fertilizer, and biodegradable emulsifier.	100 lb organism plus 400 lb fertilizer and emulsifer if needed.
		Chemical biological augmentation process	Uses chemical treatment ahead of biological treatment to shorten treatment time (currently in experimental and demonstration stages).	
Sybron Biochemical	Birmingham, NJ; Salem, VA	Detoxsol	Formulation of mutant bacteria, buffer nutrients, growth stimulator, and detoxifying agent.	363lb/acre

*Source: Sims and Bass 1984

Augmentation of biological systems with exogenous microbes (bioaugmentation) may be most effective against one compound or closely related compounds. Toxicity or the inability of the microorganisms to metabolize a wide range of substrates may limit the effectiveness of the treatment.

Table 16 lists compounds or classes of compounds that may be degraded by mutant or selected bacterial cultures that are available commercially.

Table 16. Classes of Compounds That Can Be Degraded by Commerically Available Microbial Augmentation Productions*

- Alcohols
  - n-Butyl alcohol
  - Dimethylaminoethanol
- Alkyl halides
  - Ethylene dichloride (1,2-dichloroethane)
  - Methylene chloride (dichloromethane)
  - Propylene dichloride (1,2-dichloropropane)
- Amines
  - Dimethylaniline
  - Trimethylamine
- Aromatic hydrocarbons
  - Divinyl benzene
  - Polynuclear aromatic hydrocarbons (PAHs)
  - Styrene (vinyl benzene)
- Chlorinated aromatics
  - Polychlorinated biphenyls (PCBs)
- Esters
  - Methacrylates
- Ketones
  - Acetone
- Nitriles
  - Acrylonitrile
- Phenols
  - Phenol
  - Metachlorophenol
  - Orthochlorophenol
  - Pentachlorophenol
  - Resorcinol (1,3-benzenediol)
  - t-Butylcatechol
- Crude and refined oils
- Emulsifiers
- Detergents

* Source: Sims and Bass 1984.

The potential level of treatment achievable with bioaugmentation is high if the waste constituents are susceptible to degradation by the added microorganisms and site and soil conditions are conducive to microbial activity.

Application methods are determined in consultation with the vendor of the microorganisms. They may be applied in liquid suspension or with a solid carrier. Depending on the method of application, run-on and runoff controls may be required. The ease of application depends on the trafficability of the site and the depth of contamination.

Treatment may require relatively long periods of time to complete. Excessive precipitation may "wash out" the inoculum and necessitate retreatment. If tillage is used, the susceptibility of the site to erosion will increase.

This technology has been demonstrated in the laboratory and used in several full-scale decontamination operations. Thibault and Elliot (1979, 1980) and Walton and Dobbs (1980) reported case histories of successful treatment at chemical spill sites (oil spill, orthochlorophenol spill, and acrylonitrile spill). Nevertheless, some hazardous waste cleanup practioners are skeptical about the use of this technology because of the importance of the soil environment in determining microbial activity and, hence, the success of applying exogenous organisms. More information is needed on the ability of exogenous organisms to survive, grow, and function in the soil environment.

Secondary Impacts

If tillage, is used, the site's suspectibility to erosion may increase.

Equipment, Exogenous Reagents, and Information Required

The equipment required for bioaugmentation varies according to the microorganisms used and as recommended by the vendor. Microorganisms are usually supplied by the vendors. The following information is required prior to augmentation:

- Characterization and concentration of wastes, particularly organics at site.
- Microorganisms present at site.
- Pathogenicity to susceptible populations.
- Biodegradability of waste constituents (half-life, rate constant).
- Biodegradation products (particularly hazardous products).
- Depth, profile, and areal distribution of constituents.
- Soil properties (pH, soil moisture, nutrients, oxygen content, organic matter, temperature, etc.).
- Trafficability of soil and site.
- Climate, particularly precipitation.
- Ability of the added microorganisms to survive in a foreign and possibly hostile environment and to compete for nutrients with indigenous microbial population.
- Ability of the exogenous microorganisms to move from the injection point to the location of the contaminant in the subsurface materials (saturated and unsaturated zones).
- Ability of the added microorganisms to retain their selectivity for metabolizing those contaminants for which they were initially adapted.

Advantages of Augmentation With Acclimated or Mutant Microorganisms

The advantages of this technology are as follows:

- The potential level of achievable treatment is high.
- Microbial inoculants with a broad range of metabolic capabilities are available commercially.
- Experience with this approach in both soil and aquatic systems contaminated with waste chemicals is expanding.

Disadvantages of Augmentation With Acclimated or Mutant Microorganisms

The disadvantages of this technology are as follows:

- Toxicity or the inability of the microorganisms to metabolize a wide range of substrates may limit their effectiveness.
- Excessive precipitation may "wash out" the inoculum and necessitate retreatment.
- Competition by other microorganisms and stress of soil environmental conditions may limit the longevity of the microorganisms.

3.3.2.3. Application of Cell-Free Enzymes

Enzymes produced by microorganisms, which can transform hazardous compounds to nonhazardous or more labile products, could be harvested from cells grown in mass culture and applied to contaminated soils. Industry commonly uses crude or purified enzyme extracts, either in solution or immobilized on glass beads, resins, or fibers, to catalyze a variety of reactions, including the breakdown or transformation or carbohydrates and proteins. Munnecke et al. (1982) discussed the enzymology of selected pesticide degradation and suggested that extracted (cell-free) enzymes might be used for the quick transformation of pesticides in soils. They pointed out that a bacterial enzyme preparation has been used to detoxify organophosphate pesticide waste from containers (Munnecke 1980) and that the enzyme parathion hydrolase hydrolyzed 1 percent parathion or diazinon within 24 hours in contaminated soil.

The use of gene-engineered, eukaryotic, cytochrome P-450 monooxygenase is another important new approach to dehydroxilation and detoxification of recalcitrant compounds such as polychlorinated aromatic hydrocarbons. Battelle, which is conducting studies on the production of enzymes, has stated that it is possible to produce enzymes to which an engineered protein sequence is attached at strategic locations. These introduced protein sequences will allow efficient immobilization of enzymes on inexpensive substrates or provide a means for microencapsulating the enzyme. Although techniques for producing and recovering the enzymes from bioengineered cells (*Bacillus subtilis*) have been refined somewhat, work on a process for the application of the enzymes for the destruction of hazardous wastes is still in progress.

Enzyme activity can often be preserved in environments that are not hospitable to microorganisms. Enzymes could possibly be used in soils with extreme pH and temperature, high salinity, or high solvent concentrations, i.e., in soils where microbial growth may be restricted. In milder soil environments, enzymatic hydrolysis or oxidation of a compound may make it more susceptible to decomposition by the soil microbiota (Munnecke et al. 1982).

To function outside the cell in the soil environment, an enzyme must not require cofactors or coenzymes, as such a requirement limits the application of many enzymes. Enzymes may also be chemically or biologically degraded. They may be leached out of the treatment zone, and they may be inactive or have lower activity if they are bound to clay or humus in the soil. Outside of biochemical and environmental constraints, logistics and costs for producing enzymes in large enough quantities may limit their use. Given the appropriate enzyme, if the enzyme remains active in the soil, the potential achievable treatment level is high.

Theoretically, enzymes would quickly transform hazardous compounds if they remained active in soil. After transforming the contaminants, the enzymes, being biochemical molecules, could be degraded easily and leave no hazardous byproducts in the soil. Laboratory experiments have been performed with parathion hydrolase. Paulson et al. (1984) demonstrated that complete degradation of 2000 ppm diazinon (97 percent) could be achieved in 3 weeks by using parathion hydrolase and high moisture control (actual field conditions were tested in greenhouse soil, and no leaching occurred).

Status of the Technology

Little information is available on the use of this technique in soil. No information is available on its use in the field. The reliability of this technology is unknown.

Secondary Impacts

Enzymatic degradation products may not be less hazardous than the parent compound(s). Products may be more water-soluble or mobile in the soil. If required, tillage will increase the susceptibility of the site to erosion. Depending on the application method, controls may be needed to prevent run-on and runoff.

Equipment, Exogenous Reagents, and Information Required

Power implements, tillers, and applicators are needed for application of this treatment. Enzymes are sprayed on the soil in solution or suspension or are spread with a solid carrier by use of sprayers or fertilizer spreaders.

In addition to the general information required for all the preceding biodegradation enhancement techniques, the following information is required prior to enzyme utilization:

- Cell-free enzymatic activity for transformation of the compound(s) of interest.
- Cofactor requirement of enzymes.
- Stability of enzyme under soil environmental conditions.

Advantages of the Application of Cell-Free Enzymes

The advantages of this technology are as follows:

- Offers a possible means of quick detoxification of pesticides.
- Enzyme activity can often be preserved in environments that are not hospitable to microorganisms.

Disadvantages of the Application of Cell-Free Enzymes

The disadvantages of this technology are as follows:

- Enzymes may be chemically or biologically degraded.
- They may be leached out of the treatment zone.
- If bound to clay or humus in the soil, their activity may decrease or stop entirely.
- Logistics and costs for producing enzymes in large enough quantities may limit use of this approach.

3.3.2.4. Vegetation Uptake

The ability of higher plants (i.e., seed-producing) to remove and accumulate compounds from the soil has resulted in studies for their potential use as an in situ treatment technique for both organic and inorganic compounds. The potential method of treatment by plants may occur through bioaccumulation, transformation (i.e., metabolizing the compound to nontoxic metabolites), or by adsorbing to plant roots for microbial degradation. Plant uptake of both organics and inorganics in the soil environment is influenced by numerous physical and chemical factors, including pH, clay content, cation exchange capacity, soil texture and compaction, organic matter content, plant species, and toxicity of the compound.

Uptake of compounds by plants occurs through chemical partitioning onto the external root surfaces leading to accumulation into the root with subsequent access to the vascular system of the plant (Bell 1988). In general, plant uptake of a chemical in the soil can be accomplished through the following main pathways (Topp et al. 1986):

- Root uptake into conduction channels.
- Uptake of vapor in the surrounding air by the vegetative parts of the plant.
- Uptake by external contamination of shoots by soil and dust, followed by retention in the cuticle or penetration through it.
- Uptake and transport in the oil cells of oil-containing plants (carrots, parsnips).

Most uptake by the plant will occur through the first two pathways, although the second two pathways may apply under specific conditions (e.g., uptake and transport of highly lipophilic compounds into the oil cells of oil-containing plants).

Several differences occur between the plant uptake of organic versus inorganic compounds. Uptake of elements can take place if the element exists as either a cation or anion (Ryan 1976). Several variables may influence the concentration of metals found in plants, including species, cultivar, maturity, and plant part. Bingham et al. (1975, 1976) have shown that leafy vegetables (lettuce, cress) accumulate significantly greater amounts of cadmium than do plants such as corn or wheat.

A major consideration to be addressed when assessing the uptake of inorganics is toxicity. Plant species differ significantly in their tolerance of metals, which could affect their use as an in situ treatment technique.

Plant uptake of organic compounds has also been investigated. Nonionic (organic) adsorption in the soil is largely to the organic matter that coats most particles in the soil. Several studies have shown that plant roots adsorb high levels of lipophilic pollutants from the soil which compete with existing soil organic matter. Bell (1988), Kew et al. (1989), and Facchetti et al. (1987) have shown that there is substantial accumulation of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in plant roots and tubers. This ability to collect and hold TCDD offers potential as a soil cleanup technique.

The half-life of a compound also affects ultimate plant uptake. Ryan et al. (1988) have shown that chemicals with short half-lives (less than 10 days) are removed from the system before they can be taken up by the plant. Compounds with longer half-lives (greater than 6 months or longer than the growing season) persist long enough to have potential for plant uptake.

To date, several other studies on plant uptake of pollutants have been attempted, including:

- Biotransformation of TNT (Palazzo et al. 1986).
- Uptake of organics by aerial plant parts to predict air-to-aerial vegetative transfer of organic chemicals (Travis and Hattemeyer-Frey 1988).
- Uptake of organic compounds by rice plants using C (Bahadir and Pfister 1987).
- Inverse affects of K_{ow} on uptake and bioconcentration of compounds (Travis and Arms 1988).

Status of Technology

Use of this technology for cleanup has been investigated, primarily at the laboratory level. Several studies (Bell 1988, Dowdy and Larson 1975, Shauer et al. 1980) have investigated plant uptake of organics and metals under field conditions. Further investigations of rates of uptake, toxicity, and transformation of pollutants are warranted.

Secondary Impacts

Substantial uptake of pollutants could produce toxic effects on the plant and result in harmful effects on both the plant and any animals ingesting the plant.

Equipment, Exogeneous Reagents, and Information Required

This technology would require basic agricultural techniques for growing crops. Knowledge of plant tolerances and their ability to take up and accumulate the pollutant in question would be necessary.

Advantages of Vegetation Uptake

Advantages of this treatment technique include:

- Soils can be treated without excavating large quantities of material.
- Worker exposure is minimized.
- Cost of this technology would be relatively low.

Disadvantages of Vegetation Uptake

The disadvantages of this treatment method are as follows:

- Toxicity of pollutants may have adverse effects on the plant or on animals eating the plant.
- Plants will, in most cases, only remove small amounts of the contaminant.
- Plants would need to be disposed of (e.g., incinerated) after uptake of the contaminants.

3.3.2.5. Case Histories of Bioremediation

Most large-scale bioremedial actions involve more than one of the technological approaches described in this subsection or comprise a combination of chemical/physical/biological in situ or onsite treatments. The biological treatment is often used as a polishing step. Selected examples of full-scale bioremediation projects reported in the literature are described herein. Several EPA documents contain additional descriptions of in situ applications of biodegradation and should be consulted (EPA 1984, 1986, 1988).

Formaldehyde Rail Car Spill, Ukiah, California (Sikes et al. 1984)

A strong formaldehyde solution (20,000 gallons) drained from a rail car and seeped into and through the ballast and into a drainage system. A heavy rainfall washed most of the remaining formaldehyde into the drainage system. The following mitigation operations were developed and implemented:

1) Isolation of the spill site and removal of more than 3,000,000 gallons of contaminated rainwater for offsite treatment.

2) In situ chemical oxidation of the contaminant with alkaline hydrogen peroxide (pH 9 to10), followed by biological oxidation with exogenous acclimated microorganisms.

Figure 3 presents a schematic diagram of the treatment system.

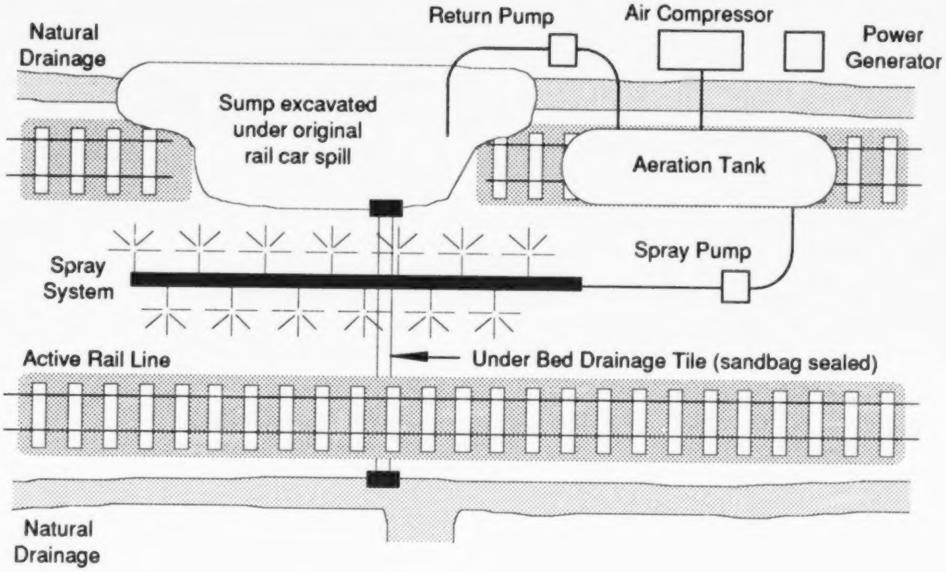
After chemical treatment, the rail ballast was converted into a trickling filter. The commercially available Hydrobac inoculum (Polybac, Inc.) was used because it was certified to contain no human pathogens. The inoculum, nitrogen-phosphate nutrients, and chemicals for pH control (sulfuric acid and soda ash) were mixed in an aboveground aeration tank, and the mixture was sprayed over the system periodically (inoculum at 3 lb/day, chemicals as needed).

After 8 days of operation, weather conditions and water evaporation in the aeration tank and spray system had dropped the low sump temperature to about 10°C. Because low temperatures could slow down the biological activity, a 1.5-million Btu/h steam-cleaning unit had to be used to maintain the optimum temperature.

After 17 days of treatment, the formaldehyde concentration at the spill site had been reduced from approximately 700 ppm to less than 1 ppm. The biological treatment was discontinued after the formaldehyde concentration was 1 ppm or less for several days, and 200 gallons of 35 percent peroxide solution was then added to the holding tank and pumped through the soil system to sterilize it.

Based on the data collected during the entire operation, it was concluded that biological oxidation was the major mechanism of formaldehyde removal at the spill site.

Figure 3. Diagram of the biological treatment process at the spill site.



Phenol-Contaminated Site in Michigan (Walton and Dobbs 1980)

The soil and ground water at this site were highly contaminated with a mixture of phenol and its chlorinated derivatives. A combination of aboveground and in situ biological treatment was selected as the remedial action.

Ground water was pumped out of the aquifer, circulated through activated carbon filters (to remove contaminants), and injected into the soil.

The natural soil microbial population was augmented with mutant bacteria. These bacteria were injected into the soil and in a containment pond holding surface runoff.

Phenol was rapidly degraded, whereas the degradation or o-chlorophenol was slower. Although the data presented did not conclusively link the degradation of contaminants to the bioaugmentation technique, a correlation between removal of contaminants and inoculation of mutant bacteria seemed to be indicated.

Biocraft Site, Waldwick, New Jersey (Jhaveri and Mazzacca 1985)

Soil and ground water at the Biocraft Site (4.5 acres) were contaminated with methylene chloride, n-butyl alcohol, dimethylaniline, and acetone. These compounds had leaked into the ground from an underground pipeline and contaminated approximately 1.75 acres. Based on the information obtained in laboratory and field studies (and with the approval of the New Jersey Department of Environmental Protection), Groundwater Decontamination Systems, Inc., designed and successfully operated a biorestoration program. The program consisted of 1) recovery of ground water downgradient of the contaminated plume by use of a collection trench and two dewatering wells; 2) aboveground aerobic biological treatment of contaminated ground water; 3) injection of air along the major pathway of the ground-water flow (by use of nine wells) to maintain aerobiosis; and 4) injection of the treated ground water upgradient of the contaminated plume by use of two infiltration trenches. The aboveground biological treatment operated as a conventional activated sludge system. In the first tank (aeration unit), air, water, nutrients, and acclimated microorganisms were mixed and maintained at the optimum temperature with a steam coil. The treated ground water then flowed to a second tank (settling tank), where the bulk of the microorganisms were settled out. The settled biomass could either be recycled to the aeration tank or discarded. The effluent, which contained residual microorganisms, nutrients, and dissolved oxygen, was infiltrated into the ground. Figure 4 presents a schematic diagram of the in situ bioreclamation system.

Water and soil analyses (COD, GC, CO_2) showed that, in 3 years, this biostimulation-degradation system had reduced the size of the original contaminated plume by 90 percent. A tenfold increase in CO_2 production in the contaminated area compared with background levels confirmed that in situ biodegradation had occurred at the Biocraft site. Although at the time of the Jhaveri and Mazzacca publication (1985), detectable levels of methylene chloride, acetone, n-butyl alcohol, and dimethylaniline still remained in the contaminated area, evidence indicated these contaminants were being rapidly degraded.

Naval Air Engineering Center (NAEC) Site, Lakehurst, New Jersey (Flathman and Caplan 1986)

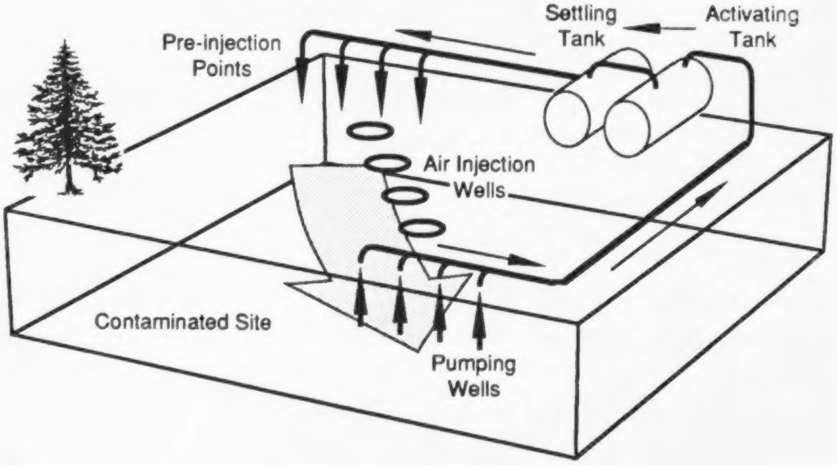
An estimated 4000 gal of cooling water (25 percent ethylene glycol) leaked from a lined surface storage lagoon and contaminated the soil and ground water with ethylene glycol.

Because feasibility study data indicated that biological treatment was a viable option for remediation of this site, O.H. Materials, Co. (Findlay, Ohio) designed and implemented a program consisting of three phases:

1) Operational: Fourteen days to achieve maximum recovery and treatment of ground water and maximum enhancement of bacterial growth in the soil/ground-water system.
2) Monitoring: Three months to evaluate the effect of nutrient addition (nitrogen and phosphate), pH adjustment, and bioaugmentation on the ethylene glycol degradation rate in the ground water.
3) Maintenance: Nine months to provide the optimum environmental conditions for biological degradation of any ethylene glycol residues remaining in the soil/ground-water system.

Ground water was recovered for aboveground treatment in an activated sludge unit. Supernatant from the settling tank was reinjected into the subsurface environment, which established a closed-loop system. Before reinjection, nutrients and chemicals were added to the treated ground water to adjust the pH so as to enhance subsurface microbial activity.

Figure 4. Schematic diagram of biological treatment system for in situ treatment of contaminated ground water at the Biocraft site.



Three injection systems were used: 1) a lagoon (to flush the contaminants from the unsaturated zone to the extraction wells), 2) a plume-injection system (to enhance bacterial growth and to create a gradient from the fringe of the contaminated plume toward the recovery wells located at the center of the plume), and 3) a surface-application system (to enhance microbial activity in the contaminated soil).

After 26 days of treatment, 85 to 93 percent of the ethylene glycol had been removed from the ground water; and by the end of the program, the level of contaminant in all production wells had been reduced to below detection limit (< 50 mg/L).

Gasoline-Contaminated Site (Yaniga and Smith 1986)

Soil and ground water at this site were contaminated with gasoline-type hydrocarbons (benzene, toluene, xylene — from less than 10 µg/L to more than 15 mg/L) and certain associated inorganic compounds (Fe, 0.1 to 6.7 mg/L; Mn, 0.2 to 12 mg/L) as a result of leakage from an underground storage tank. In this case, a 3-year combined physical/chemical/biological abatement program was implemented to treat hydrocarbons adsorbed/dissolved into the ground-water system.

Preliminary research indicated that field and laboratory *Nocardia* and *Pseudomonas* cultures were degrading the organic contaminants. Therefore, the in situ aquifer restoration program involved stimulation of the growth of the indigenous hydrocarbon degraders by adding nutrients and oxygen to the ground-water system and physical/chemical treatment to neutralize and remove metallic compounds. Ground water was pumped from a well located in the center of the contaminated plume to force the water to flow radially from the periphery. The ground water was then air-stripped to remove volatile organics and to supply oxygen. Nutrients were added to the oxygenated water before it was injected into the contaminated soil and ground water. An infiltration gallery located at the periphery of the plume (30,000 to 50,000 gal/day) was used to deliver the water. Initially, air was also injected to the peripheral areas of the plume outside the infiltration gallery by using air lines and down-well diffusers. This air-sparging system, however, was able to induce only a limited quantity of oxygen (10 mg/L) to the ground-water system, which is approximately the solubility of oxygen in water at 18°C. Also, frequent mechanical cleaning was required to eliminate fouling at the sparging points, caused by thick bacterial growth.

After 11 months of operation, this cleanup system reduced organic contaminants by 50 to 85 percent. Despite these results, the low rate of oxygen transfer was limiting the microbial growth rate and, consequently, the rate of degradation of contaminants, which lengthened the overall biorestoration time. Laboratory and field studies were conducted to find a more effective oxygen-delivery system. These studies showed that using a hydrogen peroxide solution could increase the dissolved oxygen concentration from 0.5 to 8.0 mg/L in the soil/ground-water system in a 24-hour period. When a 100 mg/L solution of hydrogen peroxide was added to the soil/ground-water system at the infiltration gallery and air sparging wells, this solution not only yielded a dissolved oxygen concentration of 50 mg/L (available for the microorganisms), but also helped to control undesirable biological growth at the well bores. The abatement program reduced the overall hydrocarbon concentration levels in the initially most contaminated area of the plume. The data collected at the site also indicated that degradation was still taking place in five of the homeowner wells in which contaminants had been detected.

Kelly Air Force Base (KAFB) Waste Disposal Site, Texas (Wetzel et al. 1986; 1987a, b, c)

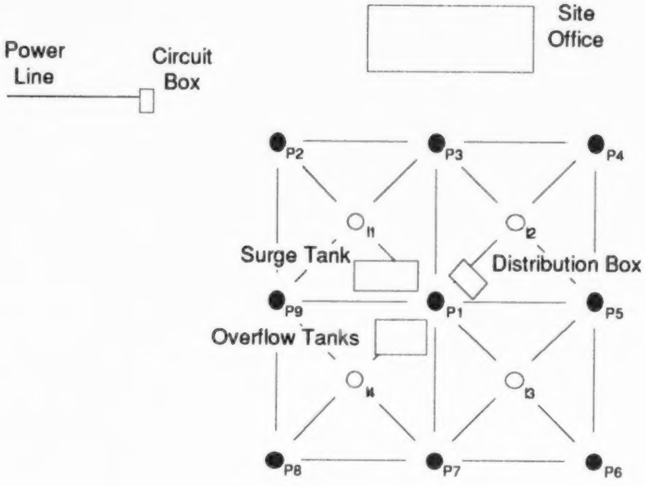
The KAFB site was originally used to dispose of chromium sludges and other electroplating wastes and later as an evaporation pit for chlorinated solvents, cresols, chlorobenzenes, and other chemicals. The effectiveness of the in situ biological treatment of the organic contaminants was tested in a small-scale field soil and ground-water system.

The design and implementation of this field demonstration project demanded extensive investigations 1) to characterize the site (site stratigraphy and hydrology); 2) to determine the extent and nature of the contamination; 3) to confirm the existence of viable bacterial population at the site and to evaluate possible correlations between the number of bacteria present and the soil type, location, and contaminant concentrations; and 4) to determine (by use of microcosms) which compounds would be degraded under which treatment conditions, and which compounds were the intermediate metabolites and metabolic products of such a degradation process.

The cleanup project involved circulation of ground water by extraction/infiltration. Ground water was pumped from the pumping wells to a central surge tank, from which it was released at a controlled rate to a distribution pipe. Along the pipe, hydrogen peroxide and specially formulated nutrient solutions were added to the circulating water to enhance biodegradation (Restore 105, Stabilized H_2O_2, and Restore 375 K Microbial Nutrients from FMC Aquifer Remediation Systems, Princeton, New Jersey). The ground water was then sent to a central distribution box, where the flow was divided for gravity injection. Figure 5 shows the configuration of the pumping and injection systems.

The results reported by Wetzel et al. (1986) were inconclusive concerning the effectiveness of the biodegradation for treating organic contaminants at the KAFB site, primarily because of the short study period (3 months). Although preliminary bench-scale investigations showed that enhancing the biochemical activity of native microorganisms could make biodegradation a feasible alternative for the KAFB site, the site stratigraphy and hydrology limited the effectiveness of such an in situ biological remediation program. Subsurface heterogeneity appeared to decrease the rate of transport of nutrients and hydrogen peroxide (oxygen source) at certain areas of the demonstration site.

Figure 5. Configuration of pumping injection system at the Kelly Air Force Base site.



Skrydstrup Chemical Waste Disposal Site, Denmark (Christiansen and Vedby 1988)

A refrigerator factory used the Skrydstrup site (approximately 15,000 m^2) to dispose of 200 tons of drums containing paint sludge and foam waste from refrigerator insulation (xylenes, butanols, oxytoles, and acetone) and drums containing sludge from the degreasing bath (oil waste), waste packaging materials, and chemical residues (chlorinated solvents such as trichloroethylene, etc.; acid residues such as hydrochloric and sulfuric acids), plastic waste from faulty refrigerators (burnt boxes), and other production waste. Severe soil and ground-water contamination was detected, especially from chlorinated solvents and some haloalkyl phosphates (from foam waste). In general, the site remediation consisted of 1) removal of drums, 2) excavation of the most contaminated spots until removal of any visible contamination, and 3) cleanup of the remaining contaminated unsaturated zone and ground water. For the accomplishment of the last step, four full-scale development projects were established to evaluate different in situ and onsite remediation technologies:

1) Biodegradation of chlorinated solvents in soil.
2) Aerobic degradation of chlorinated solvents in ground water by the addition of natural gas through activated carbon adsorption in columns.
3) Aerobic degradation in the unsaturated zone with cometabolism by oxidation of methane or propane gas.
4) Anaerobic biodegradation of chlorinated solvents in the contaminated aquifer by the addition of sodium acetate.

Only the in situ treatment of the residual chlorinated solvents in the unsaturated zone is described herein.

Although most of the source of the contamination at this site had been removed by other techniques, some chlorinated solvents remained in the soil under the site. Extracted and treated ground water was to be recycled through the excavation site to accelerate the leaching of the remaining chlorinated solvents (and other pollutants). Also, laboratory and field tests were designed to evaluate in situ aerobic biodegradation of the contaminants. The laboratory tests consisted of batch and column studies to assess the effect of 1) biostimulation (addition of nutrients), 2) augmentation (with adapted bacteria instead of natural soil bacteria), and 3) cometabolism (with different gases — methane, propane, and natural gas). Various gas/air ratios and frequencies of application (continuous vs. intermittent injection) were also evaluated. Information and principles obtained from the column studies were used in the design and conducting of the field tests. In general, the tests consisted of injection of air/gas through the unsaturated zone and infiltration of water with and without nutrients and naturally acclimated microorganisms. Gas catchment devices were installed on the soil surface to collect samples for analysis of injected gases and chlorinated solvents. Biodegradation was to be monitored during the period of the field tests (2 years). Water samples were to be taken at different depths in the unsaturated zone, and soil samples were to be taken before and after the test. No data have been reported at this writing.

Petrol Station, Asten, The Netherlands (van der Berg et al. 1987)

At this petrol station, the soil (approximately 1500 m^2) is contaminated with gasoline (approximately 30,000 liters) and a small quantity of diesel oil from a leaking tank.

Laboratory studies were conducted of the soil contaminated with gasoline and diesel oil to assess the possibility of stimulating the biological degradation of such contaminants by changing the abiotic and biotic conditions. The following parameters were evaluated: nutrient content (C-N-P ratio), nitrogen source, bioagumentation with oil degraders, addition of sodium acetate, moisture control, pH, and alternative oxygen sources (hydrogen peroxide and nitrate). In summary, the laboratory studies showed that the biological activity in the soil could be enhanced by 1) inoculation of acclimated oil-degrading bacteria, 2) maintaining saturated and neutral pH conditions, and 3) the addition of nitrate and phosphate. Mass balance calculations indicated that the rate of degradation of the gasoline in the site soil was determined by the rate at which the gasoline became available (via dissolution and volatilization processes). Soil column leaching experiments were set up for the investigation of the bioavailability problem and the effects of percolation rate, gasoline concentration in the soil, and the addition of detergents when available. These experiments showed that 1) the leaching of gasoline was hardly affected by the gasoline concentration in the soil, 2) a linear relationship existed between the total amount of organic carbon leached and the flow rate, and 3) leachability of gasoline was not promoted by detergents.

The column tests also indicated that injection of aerated water would not provide sufficient oxygen and that hydrogen peroxide could be used as an alternative oxygen source. Nitrate, on the other hand, did not appear to be a reasonable prospect. Although considerable biodegradation seems to have taken place, the actual biodegradation of contaminants and cleanup of the soil will be determined from analysis of the soil after the columns are dismantled. Based on the above results, it was estimated that the site could be cleaned up in 1.5 years by stimulating biodegradation (a degradation rate of 10 mg C/kg per day was measured under laboratory conditions). A daily throughput of approximately 1850 m^3 of water for a 625-m^2 area was also calculated and used for the design of the site remediation operation. The water will be infiltrated through drains and recovered by pumping wells (rate of withdrawal > rate of infiltration). These findings and the preliminary hydrological investigation have led the investigators in charge of the remediation program to conclude that the proposed remedial actions are technically feasible and that "in situ biological treatment offers a good alternative and some advantages over excavation combined with physical, chemical, or biological treatment."

Jet-Fuel Spill Site, Eglin Air Force Base, Florida (Downey 1988)

Approximately 100,000 liters of jet fuel leaked from an underground pipeline in the base petroleum storage area and contaminated 4000 to 5000 m^3 of soil and shallow ground water. The first cleanup operations involved removal of the free fuel by use of a series of shallow trenches filled with gravel and removal of 30,000 additional liters of fuel by use of skimmer pumps.

Because the hydraulic properties of the site and the soil characteristics were suitable for in situ bioremediation, the Air Force Engineering and Service Laboratory conducted a full-scale investigation at the site to assess techniques for enhancing biological degradation of the fuel residuals in the soil and ground water. Total petroleum hydrocarbons (TPH), TOC, and a set of representative fuel components were selected to characterize the soil and water and to monitor the degradation process. Prior to operation of the field system, laboratory studies were performed to determine the viability of the soil and ground-water microorganisms, their response to the addition of nutrients and oxygen, and their ability to degrade jet fuel.

The 2- to 3-year field study was designed primarily to evaluate the following:

1) The use of several phosphate compounds (soil conditioners) to prevent destabilization of the hydrogen peroxide used as an alternative oxygen source in the aerobic treatment.
2) Optimum nutrient and oxygen concentrations and delivery system.
3) Rate of degradation of certain components of jet fuel.

A control area upgradient of the site was used to determine natural degradation of the jet fuel. Figure 6 shows the three delivery systems used in this project.

After 3 months of applying nutrients and hydrogen peroxide, no conclusive signs of biodegradation of the jet fuel were observed (based on soil and ground-water analysis). The most important information obtained from the first 4 months of operation of the system was that, in spite of having pretreated the soil with phosphates to increase the hydrogen peroxide half-life (from 1 to 2 hours), little peroxide was being transported to the aquifer. Another report was planned for publication after 8 months of operation of the bioremediation system.

Phenolic Resin Plant, U.S.A. (Rozich and Zitrides 1988)

Over the years, soil and ground water at this site were contaminated with accidental spills of stored solvent and other chemicals. Toluene, xylene, phenol, methyl ethyl ketone, and other monomers and solvents were detected in the ground water (100 to 200 mg/L). A biostimulation system (Figure 7) was developed and operated to clean up the contaminated soil and associated ground water. The system consisted of extraction of ground water, aboveground biotreatment, and infiltration (spray application) of a portion of the bioreactor effluent containing active biomass to clean the contaminated soil. The surface biological treatment (fixed-film aerobic system) was sometimes complemented with a physical or chemical treatment to remove those pollutants that could not be removed by microorganisms (e.g., heavy metals).

The site was delisted under State regulations after 2 years of treatment.

Trichloroethane Spill Site, New Jersey (Boyer et al. 1988)

The soil and ground water at this site had been contaminated with several hundred kilograms of 1,1,1-trichloroethane (TCA) that was accidentally spilled.

Figure 6. Flow diagram of the jet-fuel spill site at Eglin Air Force Base.

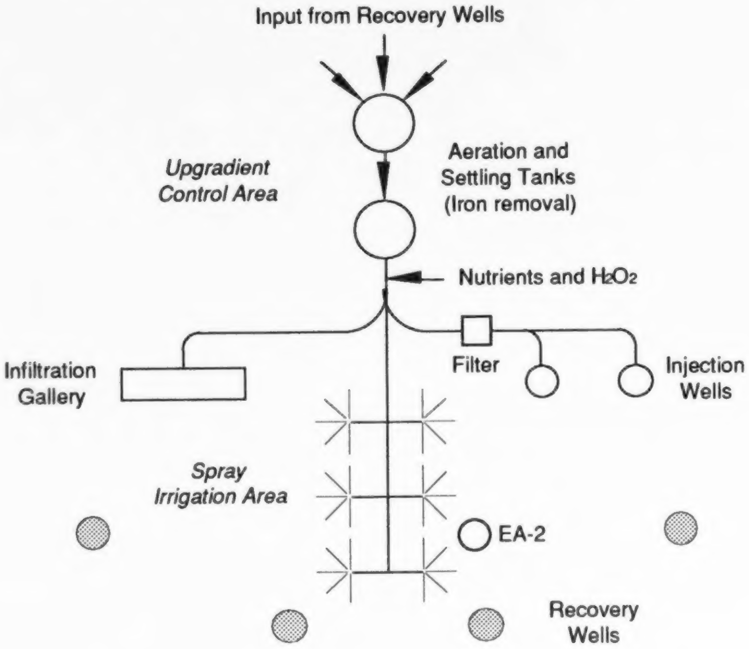
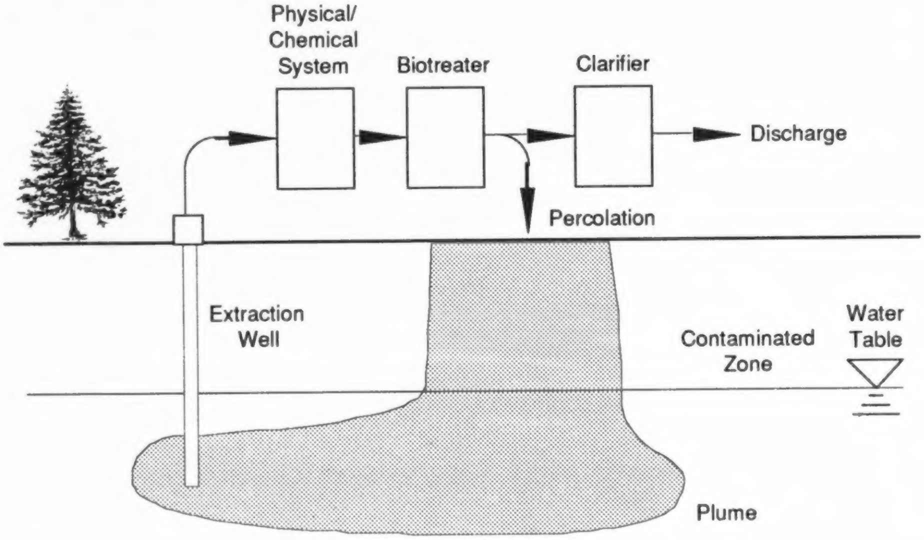
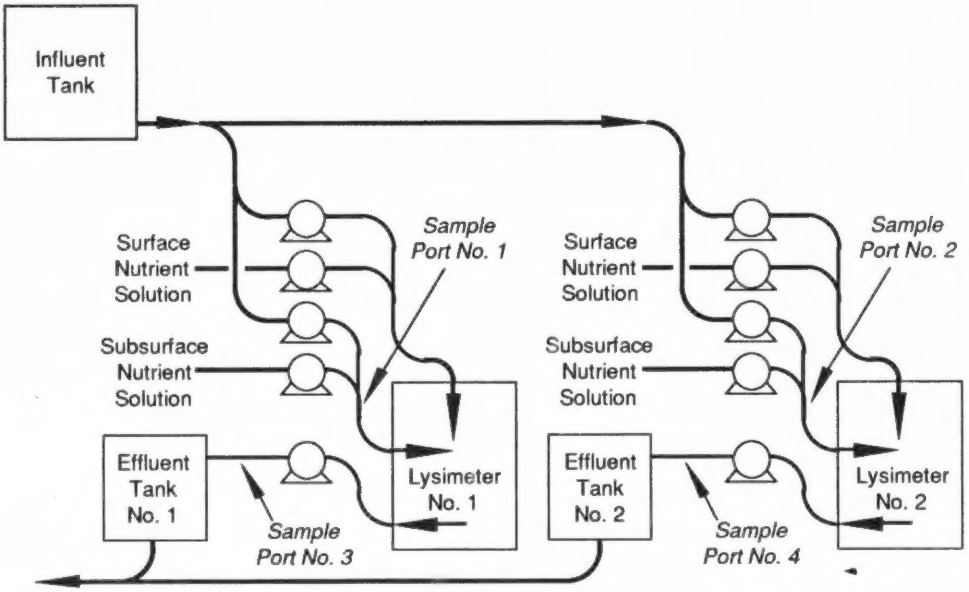

Input from Recovery Wells
Aeration and Settling Tanks (Iron removal)
Upgradient Control Area
Nutrients and H_2O_2
Infiltration Gallery
Filter
Injection Wells
Spray Irrigation Area
EA-2
Recovery Wells

Figure 7. Schematic of a biostimulation bioremediation system.


Physical/ Chemical System
Biotreater
Clarifier
Discharge
Percolation
Extraction Well
Contaminated Zone
Water Table
Plume

Based on the results obtained in laboratory studies, a pilot-scale plant was designed and constructed to evaluate an in situ aerobic/anaerobic biodegradation system. The design of the pilot plant, which was installed in the most heavily contaminated area of the site, was based on the soil column used in laboratory investigations. Figure 8 presents a flow diagram of the pilot plant. The two lysimeters were packed with contaminated soil and granular activated carbon (GAC) (5 percent). The GAC was added to facilitate flow control and to mimic the behavior of the loam at the site. Contaminated ground water was introduced into the lysimeters through surface and subsurface feed lines. While the surface feed/aerobic reaction zone prevented downward oxygen diffusion and protected the lower anaerobic zone, the subsurface feed prevented TCA losses to the atmosphere. A drainage system was used to collect the lysimeter effluents, which were then pumped into a holding tank or discarded if TCA concentrations were less than 20 ppb. The units were regularly fed with 1) a nutrient solution (nutrients, chemicals for pH control, and trace metals); 2) a surface and subsurface feed composed of glucose and ammonium sulfate (to maintain a carbon/nitrogen ratio of 10:1); and 3) a mixture of waste secondary sludge and anaerobic digestor sludge microorganisms as seed. After approximately 15 days of operation, the subsurface feed was changed to contain ethanol and ammonium sulfate (C/N ratio of 10:1). Later on, and until the end of the pilot study (6 months), a solution containing calcium nitrate, glucose or ethanol, ammonium chlorine, and monobasic potassium phosphate was used as feed. During the pilot-plant operation, some modifications in the design of the lysimeters were introduced to overcome mechanical blockage in the effluent lines. Although one of the lysimeters did not achieve acceptable flow rates, both units were equally effective in removing TCA to levels below detection (20 ppb) in the effluent at feed flow rates greater than 189 liters/day (50 gal/day). The effluents did not contain other hydrocarbons, volatile compounds, or priority organic pollutants. Based on these results, Boyer et al. (1988) concluded that "anaerobic degradation is a viable process for remediation of soil and ground water contaminated with TCA."

Figure 8. Pilot-plant flow diagram of an in situ aerobic/anaerobic biodegradation system.



3.3.3 Photolysis

Photolysis (or photodegradation) is a process that breaks down a chemical by light energy, usually in a specific wavelength range. Ultraviolet (UV) radiation is defined as electromagnetic radiation with a wavelength shorter than visible light but longer than x-ray radiation. The energy content of light increases as the wavelength decreases. The energy of the wavelengths in the UV region is sufficient to break down chemical bonds and cause rearrangement or dislocation of molecular structures. Table 17 lists the dissociation energies of common chemical bonds and the wavelength corresponding to the energy at which UV photons will cause dissociation.

Ultraviolet radiation combined with a reducing environment can dechlorinate PCBs in 1.5 to 2 hours (Wilson 1987). Because the photochemical reaction is initiated by the absorption of light energy, the irradiation wavelength must match the absorption band associated with the chemical bond of interest in the molecule, and significant absorption of the solvent must not occur at the irradiation wavelength. For PCBs, low-pressure mercury lamps that emit approximately 95 percent of their energy at 253.7 nm provide adequate irradiation (Wilson 1987).

Use of the lower atmosphere as a treatment medium requires an analysis of both the photoreaction potential and the volatility of the compounds of interest. An adequate assessment of the potential for the use of photodegradation requires information regarding the compound's atmospheric reaction rate (log $K_{OH}°$) and anticipated reaction products. This information is available for a selected number of compounds (Cupitt 1980, Lemaire et al. 1980); however, much more data are needed if photodegradation is to become a viable treatment option.

If a compound is determined to be poorly photoreactive (i.e., a $t_{1/2}$ in the atmosphere greater than 1 day), volatilization may have to be suppressed to maintain safe ambient air concentrations at the site.

Photodegradation involves the use of incident solar radiation to carry out photoreaction processes. Both direct photolysis (photoreactions due to direct light absorption by the substrate molecule) and sensitized photooxidation (photoreactions mitigated by an energy-transferring sensitizer molecule) are possible under environmental conditions. Sensitized photoreactions are characteristically ones of photooxidation that result in substrate molecule oxidation rather than substrate isomerism, dehalogenation, or dissociation, which are characteristic of direct photolysis reactions.

Studies on macroscopic sunlight attenuation at the soil surface suggest that the photolysis zone is restricted to the upper 1 to 2 mm of the soil surface. Nevertheless, field studies have shown that photochemical loss of organic chemicals may be rapid and substantial, especially in the case of hydrophobic or cationic organics that tightly sorb to the soil surface (Miller et al. 1986).

The photoreaction rate is influenced by the nature of light reaching the reaction medium, the absorption spectrum of the reacting species of the sensitizer, the concentration of reacting species, the energy yield produced upon light energy absorption, the nature of the media in which the reaction is taking place, and the interactions between the contaminant and its surroundings. Reactions are a complicated function of all these characteristics. Understanding of the photolysis reaction rates and breakdown products is very limited.

Although the soil phototreaction of adsorbed chemicals is known to occur, the importance of this reaction compared with aqueous or vapor photoreactivity has not been established. Soil photodecomposition will be of concern if the compound or compounds remain relatively stationary within the contaminated soil, e.g., high values of K_D (soil:water partition coefficient) and high values of K_w (air:water partition coefficient). Soil characteristcs, including soil organic content (Spencer et al. 1980), transition metal content (Nilles and Zabik 1975), and soil pigment content (Hautala 1978) affect photochemical reactions within soil systems. Moisture content and its effect on chemical partitioning within the air/water/soil matrix of a soil system also may have a great impact on soil photoreactions (Burkhard and Guth 1979, Hautala 1978).

Table 17. Dissociation Energies for Some Chemical Bonds*

Bond	Dissociation energy, kcal/mol	Wavelength to break bond, nm
C-C	82.6	346.1
C=C	145.8	196.1
C=C	199.6	143.2
C-Cl	81.0	353.0
C-F	116.0	246.5
C-H	98.7	289.7
C-N	72.8	392.7
C=N	147.0	194.5
C=N	212.6	134.5
C-O	85.0	334.5
C=O (aldehydes)	176.0	162.4
C=O (ketones)	179.0	159.7
C-S	65.0	439.9
C=S	166.0	172.2
Hydrogen		
H-H	104.2	274.4
Nitrogen		
N-N	52.0	540.8
N=N	60.0	476.5
N=N	226.0	126.6
N-N	85.0	336.4
N-H(NH3)	102.0	280.3
N-O	48.0	595.6
N=O	162.0	176.5
Oxygen		
O-O(O_2)	119.1	240.1
-O-O-	47.0	608.3
O-H (water)	117.5	243.3
Sulfur		
S-H	83.0	344.5
S-N	115.0	248.6
S-O	119.0	240.3

*Source: March 1985, Gray 1973, Weast and Astle 1982

Because of the relatively high volatility of pesticides and the concern for their transport via the air medium, information regarding the photolysis of pesticides in air is generally available. The major photoreaction that occurs with pesticides in the atmosphere is oxidation (Crosby 1971, Plimmer 1971) involving the OH radical or ozone, of which the OH radical is the species of greater reactivity (LeMaire et al. 1982). Based on a first-order rate of reaction of vapor phase reactions with the OH radical, the half-life of a specific chemical species can be estimated by the following equation if its OH reaction rate constant is known:

$$t_{1/2} = 0.693/(K_{OH}[OH^\circ]) \qquad (3\text{-}10)$$

where $t_{1/2}$ = Time to decrease component concentration by 50 percent, s

K_{OH} = OH radical reaction rate constant, cm^3/molecule-s

$[OH^\circ]$ = Atmospheric OH radical concentration, (4×10^5 molecules/cm^3 = 6645×10^{-19} moles/cm^3)

Table 18 presents several OH radical reaction rate constants as presented by Klopffer (1980) and Cupitt (1980). Table 19 presents additional constants as given by Cupitt (1980) and an estimation of the likelihood of a photolysis reaction occurring within the ambient atmosphere. Cupitt (1980) indicated that of all the atmospheric removal mechanisms (physical, chemical, and photochemical), the photochemical reactions are of greatest significance for most classes of hazardous compounds and should be investigated further as a viable treatment option.

Using photochemical reactions to enhance compound biodegradation is an area of interest for the mitigation of hazards at hazardous waste sites. Because photolysis reactions are oxidative in nature, they would be expected to aid in microbial degradation through the oxidation of resistant complex structures (Crosby 1971, Sims and Overcash 1983). Photoreactions are limited to soil surfaces because of the light extinction within the soil system; however, coupled with soil mixing, they may prove to be an effective in situ treatment technique for relatively immobile chemical species.

Exner (1984) proposed photolysis as a treatment option for dioxin-contaminated sites in Missouri. Experiments were carried out with mercury vapor-lamps. Within 48 hours, the dioxin in the soil was reduced by more than 90 percent. This application can be useful for decontaminating road shoulders where depth of contamination ranges from 1 to 30 cm and concentrations of dioxins range from 1 to 20 ppb. This treatment consists of the following steps:

- Disking and raking the contaminated area with agricultural equipment and using dust-supression techniques.
- Spraying the soil with a biodegradable solvent by use of a boom sprayer.
- Passing a mobile UV irradiation train over the area.
- Continuing the work until the appropriate dioxin reduction is achieved.

A photochemical treatment process was evaluated for decontamination of PCB-tainted surfaces. In a field test on concrete contaminated with Aroclor 1260 about 10 years ago, the prototype reactor destroyed 47 percent of the PCB residue after 21 hours of treatment (Draper et al. 1987). The prototype surface photoreactor was constructed of a Flexiform aluminum frame, and Westinghouse FS40 fluorescent lamps irradiated a 1.5-m^2 surface with a light intensity of 4600 $\mu W/cm^2$. Before treatment, the concrete floor was contaminated with 81 ± 31 μg Aroclor 1260/100 cm^2 ; this was reduced to 43 ±13 $\mu g/100\ cm^2$. The destruction efficiency on concrete could be improved by the following:

1) Increasing the interception of light.

2) Using a photoreactor with increased light output.

3) Using hydrogen or electron-donating solvents or photochemical sensitizers.

Photochemical reactions make up an important part of the reactions used to degrade the hazardous compounds and should be investigated further as a viable treatment option. Effectiveness of this treatment depends on the amount of tillage possible at the site, trafficability of the site, and the depth of contamination.

Various compounds can be produced by photolytic reactions, and each product must be investigated with respect to its health and environmental effects. Production of hazardous compounds from the photodegradation of pesticides has been documented, i.e., dieldrin formation from aldrin, paraoxon formation from parathion, phosgene formation from chloropicrin (Crosby 1971), and the formation of PCBs from the photoreaction of DDT (Woodrow et al. 1983).

Table 18. Rate Constants for the Hydroxide Radical Reaction In Air With Various Organic Substances*

Substance	$\text{Log}_{air}\ k_{OH}^{\circ}$†
Acetaldehyde	9.98
Acrolein	10.42
Acrylonitrile	9.08
Allyl chloride	10.23
Benzene	8.95
Benzyl chloride	9.26
Bis(chloromethyl)ether	9.38
Carbon tetrachloride	<5.78
Chlorobenzene	8.38
Chloroform	7.78
Chloromethyl methyl ether	9.26
Chloroprene	10.44
o-,m-,p-Cresol*	10.52
p-Cresol	10.49
Dichlorobromobenzene	8.26
Diethyl ether	9.73
Dimethyl nitrosamine	10.37
Dioxane	9.26
Epichlorophydrin	9.08
1,2-Epoxybutane	9.16
Epoxypropane	8.89
Ethanol	9.28
Ethyl acetate	9.06
Ethyl propionate	9.03
Ethylene dibromide	8.18
Ethylene dichloride	8.12
Ethylene oxide	9.08
Formaldehyde	9.78
Hexachlorocyclopentadiene	10.55
Maelic anhydride	10.56
Methanol	8.78
Methyl acetate	8.04
Methyl chloroform	6.86
Methyl ethyl ketone	9.32
Methylene chloride	7.93
Methyl propionate	8.23
Nitrobenzene	7.56
Nitromethane	8.81
2-Nitropropane	10.52
n-Nitrosodiethylamine	10.19
Nitrosoethylurea	9.98
n-Propylacetate	9.41
Perchloroethylene	8.01
Phenol	10.01
Phosgene	Nonreactive
Polychlorinated biphenyls	<8.78
Propanol	9.51
Propylene oxide	8.89
Tetrahydrofuran	9.95
Toluene	9.52, 9.56
Trichloroethylene	9.12
Vinylidene chloride	9.38
o-,m-p-Xylene	9.98

*Source: Adapted from Lemaire et al. (1980) and Cupitt (1980).

† K_{OH}° in units of $(\text{mole}\cdot\text{s})^{-1}$

Table 19. Atmospheric Reaction Rates and Residence Times of Selected Organic Chemicals*

Compound	$k_{OH} \times 10^{12}$ (cm^3 $molecule^{-1}$ s^{-1})	Direct photolysis probability	Physical removal probability	Residence time, days	Anticipated photoproducts
Acetaldehyde	16	Probable	Unlikely	0.03-0.7[c]	H_2CO, CO_2
Acrolein	44[a]	Probable	Unlikely	0.2	OCH-CHO, H_2CO, HCOOH, CO_2
Acrylonitrile	2	-	Unlikely	5.6	H_2CO, HC(O)CN, HCOOH, CN^o
Allyl chloride	28[a]	Possible	Unlikely	0.3	HCOOH, H_2CO, $ClCH_2CHO$, chlorinated hydroxy carbonyls, $ClCH_2COOH$
Benzyl chloride	3[a]	Possible	Unlikely	3.9	OCHO, Cl; ring cleavage products chloromethylphenols
Bis (chloromethyl) ether	4[a]	Possible	Probable	0.02-2.9[d]	$HCl+H_2CO$, ClHCO, chloromethyl-formate
Carbon tetrachloride	<0.001	-	Unlikely	>11,000	Cl_2CO, ClO
Chlorobenzene	0.4[a]	Possible	Unlikely	28	Chlorophenols, ring cleavage products
Chloroform	0.1	-	Unlikely	120	Cl_2CO, Cl^-
Chloromethyl methyl ether	3[a]	Possible	Probable	0.004-3.9[d]	Chloromethyl and methyl formate, ClHCO
Chloroprene	46[a]	Probable	Unlikely	0.2	H_2CO, $H_2C{=}CClCHO$, OHCCHO, ClCOCHO, $H_2CCHCClO$, chloro-hydroxy acids, aldehydes
o,m,p-Cresol[e]	55	-	Unlikely	0.2	Hydroxynitrotoluenes, ring cleavage products
Dichlorobenzene[e]	0.3[a]	Possible	Unlikely	39	Chlorinated phenols, ring cleavage products
Dimethyl nitrosamine	39[a]	Probable	-	<0.3	aldehydes, NO
Dioxane	3[a]	-	Unlikely	3.9	$OHCOCH_2CH_2OCHO$, OHCOCHO oxygenated formates
Dioxin	-	Probable	-	-	-

(continued)

Table 19. (continued)

Compound	$k_{OH} \times 10^{12}$ (cm^3 $molecule^{-1}$ s^{-1})	Direct photolysis probability	Physical removal probability	Residence time, days	Anticipated photoproducts
Epichlorohydrin	2^a	Possible	Unlikely	5.8	H_2CO, OHCOCHO, $ClCH_2O(O)OHCO$
Ethylene dibromide	0.25	Possible	Unlikely	45	Bi, $BrCH_2CH_2CHO$, H_2CO, Br HCO
Ethylene dichloride	0.22	Possible	Unlikely	53	ClHCHO, $H_2CClCOCl$, H_2CO, $H_2CClCHO$
Ethylene oxide	2^a	-	Unlikely	5.8	OHCOCHO
Formaldehyde	10	Probable	Unlikely	$0.1\text{-}1.2^c$	CO, CO_2
Hexachlorocyclopentadiene	59^a	Probable	-	0.2	Cl_2CO, diacyclchlorides, ketones, Cl.
Maleic Anhydride	60^a	Possible	Possible	0.1	CO_2, CO; acids, aldehydes and esters which should photolyze
Methyl chloroform	0.012	Possible	Unlikely	970	H_2CO, Cl_2CO, Cl.
Methylene chloride	0.14	Possible	Unlikely	83	Cl_2CO, CO, ClHCO, Cl.
Methyl iodide	0.004^a	Possible	Unlikely	2900	H_2CO, I^o, ICHO, CO
Nitrobenzene	0.06^a	Possible	Unlikely	190	Nitrophenols, ring cleavage products
2-Nitropropane	55^a	Possible	Unlikely	0.2	H_2CO, CH_3CHO
N-Nitrosodiethylamine	26^a	Probable	-	<0.4	Aldehydes, nitroamines
Nitrosoethylurea	13^a	Possible	-	<0.9	Aldehydes, nitroamines
Nitrosomethylurea	20^a	Possible	-	<0.6	Aldehydes, nitroamines
Nitrosomorpholine	28^a	Possible	-	<0.4	Aldehydes, ethers
Perchlorethylene	0.17	Possible	Unlikely	67	Cl_2CO, $Cl_2Cl(OH)COCl$, ClO
Phenol	17^a	-	Possible	0.6	Dihydroxybenzenes, nitrophenols, ring cleavage products

(continued)

Table 19. (continued)

Compound	$k_{OH} \times 10^{12}$ (cm^3 molecule^{-1} s^{-1})	Direct photolysis probability	Physical removal probability	Residence time, days	Anticipated photoproducts
Phosgene[f]	~0	-	Possible	-	CO_2, ClO, HCl
Polychlorinated biphenyls	<1[a]	Possible	Unlikely	>11	Hydroxy PCB's, ring cleavage products
POM (benzo(a)-pyrene)	-	Possible	Probable	8	B(a)P-1,6-quinone
Propylene oxide	1.3	-	Unlikely	8.9	$CH_3C(O)OCHO$, $CH_3C(O)CHO$, H_2CO, $HC(O)OCHO$
Toluene	6	-	Unlikely	1.9	Benzaldehyde, cresols, ring cleavage products, nitro compounds
Trichloroethylene	2.2	Possible	Unlikely	5.2	Cl_2CO, ClHCO, CO, Cl·
Vinyllidene chloride	4[a]	Possible	Unlikely	2.9	H_2CO, Cl_2CO, HCOOH
o-,m-,p-Xylene	16	-	Unlikely	~0.7	Substituted benzaldehydes, hydroxy xylenes, ring cleavage products nitro compounds

· Source: Cupitt (1980)

[a] Rate constant by method of Hendry and Kenley (1979).

[b] Material is not expected to exist in vapor phase at normal temperatures. Residence time calculation assumes the chemical is substantially absorbed on aerosol particles and that the aerosol particles have a residence time of approximately 7 days.

[c] The shorter residence time includes a photolysis rate as given in Graedel (1978).

[d] Decomposition in moist air is expected. The shorter residence time includes the cited decomposition rate.

[e] Values given are averages for the various isomers.

[f] Reaction with O('D) is possible; $k = 3.6 \times 10^{-10}$ cm^3/molecule/s, and [O('D)] = 0.2 molecules/cm^3 implies a tropospheric lifetime of 440 years. In addition, slow hydrolysis is expected.

Also, the effectiveness of this treatment depends on the amount of tillage possible at the site and the effect of any contaminants produced by photolytic reactions. A major drawback in treating soil via photolysis is the lack of penetration depth of ultraviolet radiation. In some cases, cultivators have been suggested and used to expose the contaminated material to UV light. Treatment of soil not exposed to sunlight has been attempted with banks of low-pressure mercury lights in conjunction with a surface pretreatment consisting of the application of a hydrogen donor. Run-on and runoff controls may be necessary to manage the drainage and erosion.

Photolysis of soil contaminants may be enhanced in two ways: 1) by adding photoenhancement agents, and 2) by enhancing volatilization leading to photodegradation.

3.3.3.1 Addition of Photoenhancement Agents

Certain compounds (e.g., ozone and hydrogen peroxide) are degraded to form reactive radical species (hydroxyl, peroxy, and hydroperoxy radicals and singlet oxygen) and thus enhance photochemical reactions. Gohre and Miller (1986) reported that singlet oxygen is a likely reactant in the photooxidation of sulfur-containing pesticides on soil surfaces because it is produced on both irradiated inorganic metal oxides and irradiated soils (e.g., alumina and silica gel).

Photodegradation of soil contaminants may be enhanced by adding various proton donor materials to the contaminated soils. Solvents used as hydrogen donors include alcohols, water, and hydrocarbons. In heavy hydrocarbons, polymerization of the biphenyl radicals to yield polyphenylenes is the major PCB reaction. In basic alcohol solutions, a stepwise dechlorination of the molecule occurs. These photochemical reactions yield only biphenyl and sodium chloride as the final products.

Crosby et al. (1971) reported photolysis of tetrachlorodibenz-p-dioxin (TCDD) on soil surfaces in the presence of suitable hydrogen sources in the form of polar solvents. Plimmer and Klingebiel (1973) indicated that methanol used as a solvent for TCDD photooxidation also acted as a hydrogen donor in the photolysis reaction.

Several authors have reported on investigations of feasible in situ treatment methods for contaminated areas surrounding a TCDD release that occurred near Seveso, Italy, in 1976. Wipf et al. (1978) investigated the use of alternative hydrogen donors for the photooxidation of TCDD. Solutions of 80 percent olive oil and 20 percent cyclohexane at 350 L/ha and 40 percent aqueous emulsion with 4 percent biodegradable emulsifying agent at 400 L/ha were found to produce a thin film on vegetation and other smooth surfaces suitable for maximum reaction of TCDD photolysis. Within 48 hours after treatment, TCDD reductions in excess of 60 percent were observed. Under laboratory conditions, the oil and emulsion solutions reduced the half-life of TCDD by a factor of 25 upon irradiation with simulated sunlight.

Liberti et al. (1978) reported the use of a 1:1 solution of ethyl oleate and xylene as hydrogen donors also resulted in complete degradation of TCDD on building surfaces in approximately 1 hour at 2 mW/cm^2 light intensity and 72 hours at 20 $\mu W/cm^2$ light intensity.

Dehalogenation of kepone (Dawson et al. 1980) and enhanced PBB (Christensen and Weimer 1979) photolysis have been reported when hydrogen donors in the form of amino groups were added to contaminated soils prior to irradiation with sunlight; however, no observable degradation of PCBs in soil was found with amine-enhanced soil (Meuser and Weimer 1982).

Occhiucci and Patacchiola (1982) reported soil photodecomposition of PCBs. This photodecomposition was shown to be enhanced by the addition of a proton donor, triethylamine, to the waste/montmorillonite system. Adding triethylamine resulted in a 2.5- to 5-fold increase in PCB degradation over a 100-hour irradiation period and provided 4 to 18 percent decomposition of the various chlorinated species tested.

These dechlorination reactions result from hydrogen abstraction by organic radicals formed upon irradiation (Bunce1982). This process has not yet been optimized for soil systems, but it appears to have potential for use in the in situ treatment of stable, nonmobile compounds.

Activated carbon adsorption of organics at hazardous waste sites followed by chemical addition and photolysis was reported (Sims et al. 1986). This technology involves impregnating the site with activated carbon and then sampling the soils. The most highly contaminated materials are physically removed, packaged, and disposed of in an approved hazardous waste disposal facility. The remaining material is mixed with sodium bicarbonate to increase soil pH and then allowed to react photochemically, which results in the photolysis of the parent material. The level of treatment achieved is expected to be high to medium.

Semiconductor powders and colloids, which are inexpensive, nontoxic, and recyclable, have been shown to enhance photodegradation (Sukol 1987). Titanium dioxide is the best of these photocatalysts because it can absorb a wide range of solar spectrum wavelengths more efficiently than organic contaminants can by direct photolysis.

Minerals rich in manganese, iron, and titanium oxides can be relatively abundant in soils. Transformation of certain types of xenobiotics are affected by the redox reactions on the surface of these metal oxides.

Natural sediments and clays have also been studied for their application as photosensitizing agents, and it has been reported that low levels of humic substances actually catalyze photodegradation by UV/ozonation.

Surfactants may improve photodegradation rates by enhancing the solubility of the compounds. Exner (1984) showed that irradiation of dioxin-contaminated soil in the presence of surfactants can reduce the concentration of dioxin by 90 to 99 percent within 24 hours.

Photodegradable organic wastes are amenable to this treatment. Generally, these include compounds with moderate to strong absorption in the >290-nm wavelength range. Such compounds generally have an extended conjugated hydrocarbon system or a functional group with an unsaturated hetero atom (e.g., carbonyl, azo, nitro). Groups that typically do not undergo direct photolysis include saturated aliphatics, alcohols, ethers, and amines. Tetrachlorodibenz-p-dioxin (TCDD), kepone, and PCBs have been treated with this method.

Status of the Technology

Some field testing and evaluation of the use of photoenhancement agents to promote photodegradation is ongoing (Sims et al. 1986). In addition, research is being conducted on an in situ diffusion method for enhancing the mobility of haloaromatics in the soil and increasing their movement to the soil surface for subsequent photodegradation. Investigations are continuing on the use of ethyl oleate and hexadecane for this application, and the preliminary results are encouraging (Overcash et al. 1986).

Exner (1984) reported preliminary experiments (no field study) of in situ detoxification of dioxin-contaminated soil by irradiation with UV light in the presence of organic solvents and aqueous surfactant emulsions. Spraying the soil with 0.5 to 3 percent w/w of organic surfactants and irradiation with a mercury vapor lamp reduced the dioxin concentration from 671 ng/g to 11 ng/g (a 98 percent reduction) within 31 hours. The results show that solubilization of dioxin is the primary step for in situ photolysis of the soil. Also, it was reported that the use of organic solvents is not necessary; aqueous surfactant solutions can be used instead.

A method that uses light generated by ordinary incandescent light bulbs, which is absorbed by a common dye sensitizer, has been developed for the photoreduction of PCBs to biphenyls. The dye molecules can promote a chemical reaction between polychlorinated biphenyls and a hydrogen gas such as propane (Stallard 1988). In this reaction, hydrogen is abstracted from the hydrocarbon molecule and is substituted for chlorine on the PCB molecule, which yields the reaction product biphenyl. The reaction occurs in polar aprotic solvent at room temperature and in the presence of an alkali metal hydroxide. This process could be applied to the treatment of PCB-contaminated transformer oils, soils, and landfill leachates.

Secondary Impacts

The addition of photoenhancement agents (i.e., proton donors) may change the soil pH and affect the natural microbial populations. Soil pH controls may need to be applied.

Equipment, Exogenous Reagents, and Information Required

Cultivators, equipment for diking and raking, boom sprayers, or some other sprinkling system may be required to apply the photoenhancement agents to the soil. Reagents may include singlet oxygen and hydrogen donor solvents, such as water, methanol, ethyl oleate, xylene, amino groups, and triethylamine; semiconductor powders; natural sediments and clays; metal oxides (e.g., manganese, iron, and titanium oxides); and surfactants.

The following information is required prior to the use of photoenhancement agents to effect photodegradation:

- Characterization and concentration of wastes, particularly organics, at site.
- Absorption spectra of waste constituents (at wavelengths >290 nm, molecular absorptivities, absorption maxima, quantum yield).
- Atmospheric reaction rate of compounds (log K_{OH}°).
- Photolysis rate constant(s).
- Products of photolysis and expected reaction products (particularly hazardous products).
- Volatility of organics (vapor pressure, Henry's law constant).
- Depth, profile, and areal distribution of contamination.
- Light intensity at site.
- Trafficability of soil and site.

Advantages of Applying Photoenhancement Agents

The advantages of this technique for the in situ treatment of soils are as follows:

- Reagents are inexpensive and recyclable.
- The treatment is effective on relatively immobile organic chemical species, such as a dioxin- or PCB-contaminated soil.

Disadvantages of Applying Photoenchancement Agents

The disadvantages of this technique are as follows:

- The depth of treatment is limited to approximately 1 to 3 mm below grade.
- Understanding of the photolysis reaction rates and breakdown products is limited.

3.3.3.2 Enhancement of Volatilization

Enhancing volatilization of compounds from the soil that are susceptible to photodegradation may be a potential treatment technique. This technique involves increasing the bulk density or drying of the soil system to increase soil vapor pore spaces and, subsequently, the vaporization rate of the desired compounds, followed by their photodegradation in air.

Unlike photoreactions in solution, the photolysis rate constants of hydrophobic organics sorbed on soil surfaces show a decrease with increasing irradiation. This behavior has been observed in the volatilization of pesticides from soil surfaces. This unusual behavior in kinetics may be partly due to the intraparticle transport of a portion of the organic substrate into aggregate interiors, where it is protected from sunlight or from volatilization. These results indicate that it is probably meaningless to describe the loss of PCDD or other hydrophobic organics in soils in terms of a first-order half-life (Miller et al. 1986).

Some important factors that influence volatilization of organics from the soil surface are concentration of the chemicals in the soil, chemical properties such as solubility and vapor pressure, soil water content, and water evaporation rate. Henry's law constant, K_h, which denotes the ratio between the vapor pressure of a compound and its solubility in water at a given temperature, gives an indication of the ease with which a compound may be stripped from the soil or water.

Temperature strongly affects volatilization at the soil surface. Studies of the soil temperature profiles have shown that the top few centimeters undergo pronounced diurnal and seasonal variations. In experiments with well-mixed dioxin-contaminated soil from Times Beach, Missouri, significant loss of the compound was observed within the top 3 mm from the soil surface, especially when the soil was damp. It has been proposed that these results indicate that evapotranspiration processes are important for moving PCDDs to the surface, where they undergo surface photolysis or volatilization (Miller et al. 1986).

The technique is applicable to compounds of low water solubility, with low K_D values and low K_W values, and those that are highly photoreactive and that, once within the lower atmosphere, would have a relatively short life (on the order of hours or preferably minutes).

Techniques for enhancing contaminant volatilization are discussed in detail in Section 3.4.

3.4 Control of Volatile Materials

Controlling volatilization of contaminants from a hazardous waste site is often necessary to prevent or reduce air emissions. In situ treatment technologies suitable for this purpose include reducing the rate of volatilization through physical and/or chemical means and increasing the rate of volatilization for more efficient and effective management of vapors that could be released into the atmosphere.

Volatilization from a hazardous waste site may have to be controlled to reduce air emissions. Three technologies may be used to reduce volatilization or volatile materials from a contaminated site: 1) soil vapor extraction (including vacuum extracting and steam stripping), 2) radio frequency heating, and 3) soil cooling.

3.4.1 Soil Vapor Extraction

Concentrations of volatile materials can be reduced by the use of various vapor extraction systems. Vapor extraction systems involve the recovery of volatile contaminants by injecting air into contaminated soils and extracting the air (in which volatile chemicals have partitioned) in a vapor recovery well. A vacuum apparatus is typically used to extract the volatilized contaminants.

3.4.1.1 Vacuum Extraction

Vacuum extraction processes have proved to be an effective method of controlling fugitive emissions of vaporized contaminants from uncontrolled hazardous waste sites, and are the most commonly used in situ remedial technology (Murdoch et al. 1988). Soil vapor extraction systems involve the extraction of air containing volatile contaminants from unsaturated soils. Clean air is injected into the contaminated soils, and a vacuum apparatus is used to extract the vapor-filled air from recovery or extraction wells (Hutzler et al. 1989). The operation involves the use of an air blower, and the inducted air flows come into equilibrium with extracted air. The established air flows are a function of the equipment used and soil characteristics, including soil air permeability (Hutzler et al. 1989).

The pore space of unsaturated soils is composed of liquid and vapor phases in equilibrium. Contaminants with high vapor pressures partition into the vapor phase in the air-filled pore spaces. With vapor extraction systems, these partitioning characteristics of volatile contaminants are used to facilitate their extraction when a vacuum is applied to the soil. This results in the liquid-phase contaminants being volatilized to maintain the liquid-vapor phase equilibrium present in the soil strata.

The use of vapor extraction systems is typically limited to permeable unsaturated soils such as sands, gravels, and coarse silts; diffusion rates through dense soils, such as compacted clays, are much lower than through sandy soils (USEPA 1988). Clayey soils usually lack the conductivity necessary for effective vapor extraction, unless they are first fractured. Hydraulic fracturing, a method used to increase fluid flow within the subsurface, may increase the effectiveness of vapor extraction (Murdoch 1989). Hydraulic fracturing is discussed in Section 4.1.

Vapor extraction systems may be designed to have flexible operational parameters. These include air extraction rates, extraction-well spacing and configuration, control of water infiltration, and pumping deviations (Hutzler et al. 1989). Higher flow rates increase vapor removal, as more air is forced through the permeable soil layers. Although additional wells allow a greater measure of air flow control, they also increase costs. Temporarily stopping the flow of air from the air-forcing blowers allows time for chemicals to diffuse into the vapor phase, and venting will subsequently remove higher concentrations of volatile contaminants (Hutzler et al. 1989).

Glynn and Duchesneau (1988) assessed the soil vapor extraction system used at a Belleview, Florida, site with leaking underground storage tanks (USTs). The soil had been contaminated with gasoline and other hyrocarbons and with gasoline components, including benzene, xylene, ethyl benzene, and toluene. The contaminants at this approximately 50-acre site had migrated to and contaminated the city well field, which the city subsequently abandoned. A vapor extraction system was implemented to reduce the concentrations of gasoline and gasoline components in the soils surrounding the USTs responsible for the contamination.

In a 25-day period, the vacuum extraction system removed 90 kg of total hydrocarbons from the contaminated area. The soil gases extracted from the site showed decreasing concentrations of volatile organics as time passed, which indicates that concentrations of gasoline components were being decreased. Glynn and Duchesneau (1988) found that the concentration ratio between each gasoline component tested (benzene, toluene, ethyl benzene, and xylene) varied over the 25-day field demonstration of the soil vapor extraction system. Because of their high volatility, benzene and toluene concentrations in the extracted gasses decreased faster than the other compounds. This led to the conclusion that highly volatile compounds are removed at a faster rate than less volatile compounds.

In situ vacuum extraction by a process developed by Terra Vac, Inc., has been demonstrated and evaluated as part of the Superfund Innovative Technology Evaluation (SITE) Program. Figure 9, a process diagram for this in situ vacuum extraction process, shows the extraction well, vapor/liquid separation, and the vapor treatment train. Recovery rates ranging from 20 to 2500 pounds per day are said to be obtained from the Terra Vac system; they are a function of the volatility of the organic compound recovered (USEPA 1988). During the SITE Program demonstration at Groveland, Massachusetts, approximately 1300 pounds of volatile organic compounds were extracted during a 56-day operating period (USEPA 1989).

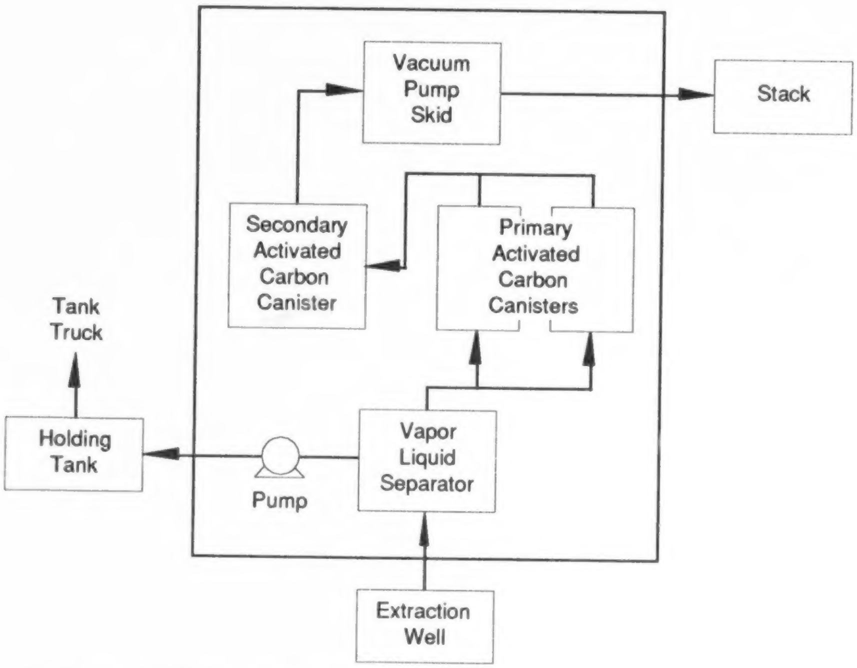
Status of the Technology

In situ vacuum extraction is being implemented in many locations across the United States. One example is the Verona Wells Superfund Site in Battle Creek, Michigan, in EPA Region V. This site contains trichloroethylene contamination (USEPA 1988). The technology has also been demonstrated at a Superfund site in Puerto Rico, where carbon tetrachloride had leaked from an underground storage tank. The SITE Program demonstration of the Terra Vac process was conducted at the Valley Manufactured Products Company, Inc. property, which is part of the Groveland Wells Superfund Site in Groveland, Massachusetts (USEPA 1989). Trichloroethylene was the main contaminant at that site.

Secondary Impacts

This technology has very few secondary impacts, as only blower-induced air is introduced into the contaminated soils.

Figure 9. Process diagram of an in situ vacuum extraction process.


Vacuum Pump Skid
Stack
Secondary Activated Carbon Canister
Primary Activated Carbon Canisters
Tank Truck
Holding Tank
Pump
Vapor Liquid Separator
Extraction Well

Equipment, Exogenous Reagents, and Information Requirements

Equipment required for soil vapor extraction systems includes air blowers, injection wells, extraction wells, a vacuum apparatus, and a carbon adsorption system to adsorb extracted vapors. No exogenous reagents are required for soil vapor extraction systems.

The following information is needed to operate this technology:

- Characterization of wastes, primarily volatile organics.
- Volatility of organic contaminants (vapor pressure, Henry's law constant, air/water partition coefficient, solubility).
- Depth, profile, and areal distribution of contamination.
- Soil matrix properties (permeability, porosity, organic carbon content, soil moisture content, and particle size distribution).
- Accessibility of soil and site.

Advantages of Vacuum Extraction

One advantage of a soil vapor extraction system is that it does not require the addition of reagents that must be delivered to and subsequently recovered from the contaminated area. The extraction system is used to remove contaminated vapor only. Also, this technology provides permanent remedial action; i.e., the contaminated soils are actually cleaned, not just contained along with the hazardous contaminants.

Disadvantages of Vacuum Extraction

A disadvantage of this technology is that the soils must be permeable and fairly homogeneous for it to be most effective. Impermeable soil lenses within more permeable soils could adversely affect the recovery of volatile soil contaminants.

Another disadvantage is that a single site containing wastes of varying volatility may require additional technologies for remediation, as vapor extraction techniques are most amenable for highly volatile compounds.

3.4.1.2 Steam Stripping

In situ steam stripping of contaminants from soil involves injecting steam into the soil beneath the contaminated zone. When assisted by a vacuum at the ground surface, steam stripping brings the contaminants to a collection point for further treatment. Lord et al. (1989) conducted a field test of this technology that included a unique geosynthetic cap and a geomembrane for containment of the steam and contaminant.

Steam stripping is particularly effective on alkanes and on alkane-based alcohols such as octanol and butanol (Lord et al. 1989). The vapor pressure and polarity of the compounds are important in determining the amenability of the compound to steam stripping; however, the exact correlation is not fully understood (Lord et al. 1989).

Status of the Technology

Bench- and field-scale studies have been conducted of in situ steam stripping of contaminated soil (Lord et al. 1989; Lord et al. 1988; Hilberts 1985; Baker et al. 1986). Further investigation of the technology is needed for a better understanding of its applicability to various chemicals and soil types.

A portable treatment unit called a "Detoxifier" is used for in situ steam and air stripping. This unit is being evaluated as part of EPA's SITE Program (Ghassemi 1988). The drills are modified to allow the injection of steam and air into the soil through the cutting blades. The ground area being drilled is covered by a containment system to trap and recover the stripped volatiles.

In this process, steam is piped to the top of the drills and injected through the cutting blades. The steam heats the ground being remediated, which increases the vapor pressure of the volatile contaminants and the rate at which they can be stripped. Both the air and the steam serve as carriers to convey these contaminants to the surface. The shroud, a metal box designed to seal the process area above the rotating cutter blades from the outside environment, collects the volatile contaminants and ducts them to the process train. In the process train, the volatile contaminants and the water vapor are removed from the off-gas stream by condensation. The condensed water is separated from the organics by distillation, filtered through activated carbon beds, and subsequently used as makeup water in a cooling tower. Figure 10 presents a process flow diagram of this treatment system.

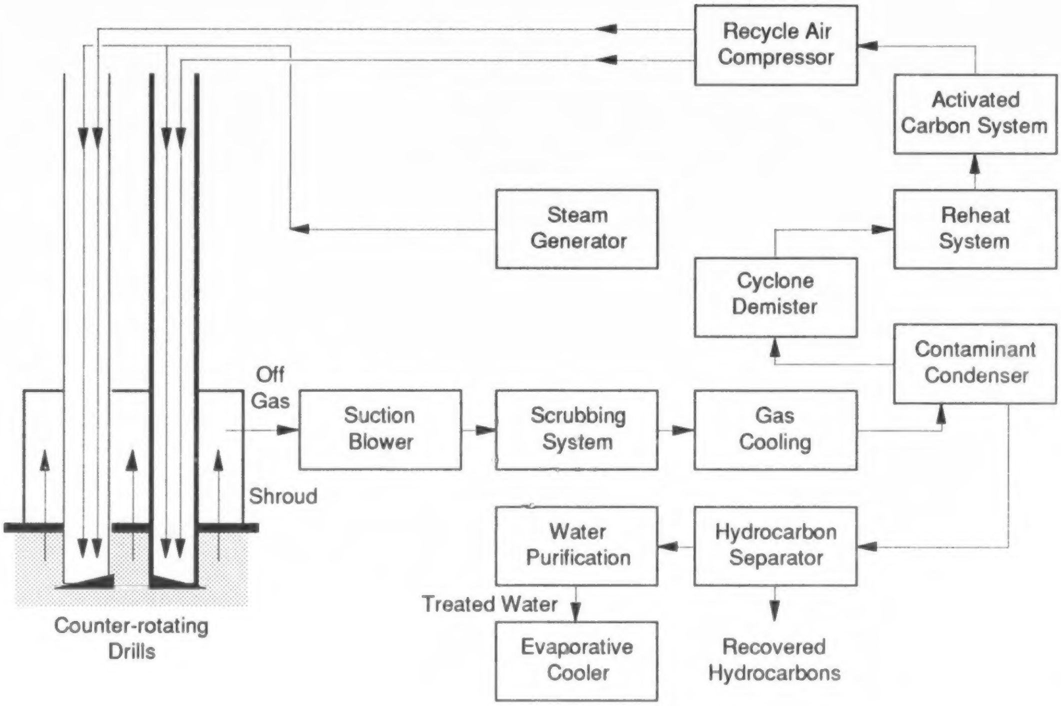
Secondary Impacts

The introduction of steam to the subsurface increases the temperature of the soil, which may either increase microbial activity or destroy some microbial populations.

Equipment, Exogenous Equipment, and Information Required

In situ, vacuum-assisted, steam stripping requires steam injection pipes, a vapor containment system (geomembrane), and a vacuum collection system. A steam generator is also required.

Figure 10. Process flow diagram of an in situ steam stripping process.


Recycle Air Compressor
Activated Carbon System
Steam Generator
Reheat System
Cyclone Demister
Contaminant Condenser
Off Gas
Suction Blower
Scrubbing System
Gas Cooling
Shroud
Water Purification
Hydrocarbon Separator
Treated Water
Counter-rotating Drills
Evaporative Cooler
Recovered Hydrocarbons

Information necessary for the effective design and application of an in situ steam-stripping system includes the following:

- Depth and areal extent of contamination.
- Depth to ground-water table.
- Vapor pressure and polarity of organic contaminants.
- Subsurface stratigraphy, including the presence of clay lenses.

Advantages of Steam Stripping

Steam stripping to extract contaminants from the soil has the following advantages:

- Alkanes and alkane-based alcohols are effectively extracted from soils.
- The treatment time can be as short as several hours, depending on the extent and amount of contamination.

Disadvantages of Steam Stripping

Steam stripping has the following disadvantages:

- The increase in soil temperature may adversely affect other soil properties.
- Not all the mechanisms of the technology are fully understood.

3.4.2 Radio Frequency Heating

Many Superfund sites are contaminated with various solvents and fuels. Aliphatic and aromatic fractions of jet fuels and gasoline, chlorobenzene, trichloroethylene, dichloroethane, and tetrachloroethylene are some of the contaminants found at contaminated sites. These compounds pose a considerable environmental threat, as they could migrate from the site and contaminate drinking water supplies. Materials that typically volatilize in the temperature range of 80° to 300°C (such as those just listed) may be more easily recovered in extraction systems if the soil temperature is raised to increase the volatilization rates. Radio frequency heating is one method of soil heating for contaminant removal.

Radio frequency (RF) heating is a technique for rapid and uniform in situ heating of large volumes of soil (Dev et al. 1988). This technique heats the soil to the point where volatile and semivolatile contaminants are vaporized into the soil matrix. Vented electrodes are then used to recover the gases formed in the soil matrix during the heating process. The concentrated extracted gas stream that is recovered can be incinerated or subjected to other treatment methods.

Radio frequency heating is accomplished by the use of electromagnetic energy in the radio frequency band (Dev et al. 1988). The energy is introduced into the soil matrix by electrodes inserted into drilled holes. According to Dev et al. (1988), the mechanism of heat generation is similar to that of a microwave oven. The heating process does not rely on the thermal conductivity of the soil. A modified radio transmitter serves as the power source, and the industrial, scientific, and medical (ISM) band provides the frequency at which the modified transmitter operates. The exact operational frequency is obtained from an evaluation of the areal extent of contamination and the dielectric properties of the soil matrix (Dev et al. 1988).

The frequencies used during RF heating remedial work may be as low as 45 Hz or as high or higher than 10 GHz. The frequency range for most RF heating applications at hazardous waste sites is between 6.78 MHz to 2.45 GHz (Dev et al. 1988).

Full implementation of an RF heating system at a contaminated hazardous waste site requires four major subsystems: 1) an RF energy deposition array; 2) RF power generating, transmitting, monitoring, and control systems; 3) a vapor barrier and contaminant system; and 4) a gas and liquid condensate handling and treatment system. The electrode array (also known as the exciter array) design is the critical system that determines the design and operational parameters of the other systems.

During installation of RF heating systems, electrodes are placed in three parallel rows that form two outer walls and a single central conductor. Demonstration has shown that appropriate spacing of the electrodes within each row and the rows themselves allow the applied electromagnetic field to be contained within the outer "walls" of electrodes (Dev et al. 1988).

A field demonstration test was conducted at the Volk Air National Guard Based at Camp Douglas, Wisconsin. For more than 25 years this site had been used as a fire-fighting training area, where waste oils, fuels, and other hydrocarbons were dumped into a pit and ignited to simulate aircraft fires. An estimated 50,000 gallons of waste hydrocarbons had migrated into the soil in and around the pit (USDOE 1988). This site offered the homogeneous waste and soil characteristics necessary for a controlled test of the RF heating technology. The complete system included a cooler/condenser, a gas-liquid separator, and a carbon adsorption unit for trapping the vented gas stream. Condensed liquids were collected and saved for later analysis.

The soil temperature reached 100°C after 2 days of inducting the radio frequency waves into the soil, and 150°C after 8 days of RF heating (Dev et al. 1988). The test was completed after 12.5 days of RF heating. The results presented in Table 20 show that RF heating decreased the relative levels of contamination at this site. The method was especially effective for removal of volatile organics. As shown, this technology is suitable for treating both volatile and semivolatile organic contaminants in soils. Treatment levels are potentially high, depending on the waste characteristics and the homogenity of the contaminated soil. The best treatment levels could be expected in predominantly sandy soils. Application of this technology could be hindered if the soil characteristics caused the drilling of soil borings to be difficult.

Table 20. Percent Reduction of Contaminants From RF Heating of Soil*

Depth interval, inches	Moisture	Aliphatics		Aromatics	
		Volatile	Semivolatile	Volatile	Semivolatile
6-72	97.2	99.3	94.3	99.6	99.1
6-12	96.1	98.2	88.1	99.2	98.1
30-42	96.1	99.7	97.6	99.6	99.6
60-72	98.9	99.8	98.5	99.9	99.9

* Source: Dev et al. 1988.

3.4.2.1 Status of the Technology

Radio frequency heating is a new technology for cleanup of hazardous waste sites. It is currently in the pilot- and field-scale demonstration stage and has been tested at the Volk Field ANGB, Wisconsin in cooperation with the U.S. Department of Defense, U.S. EPA, and the Illinois Institute of Technology Research Institute.

3.4.2.2 Secondary Impacts

The high soil temperatures associated with this technology would inhibit or destroy existing colonies of microbes in the soil matrix. The high temperatures could also have an adverse effect on humic matter within the soil matrix.

3.4.2.3 Equipment, Exogenous Reagents, and Information Required

Equipment requirements include a transmitter, a power source, electrodes, ancillary equipment for gas extraction and containment, and soil boring devices. No exogenous reagents are required for this technology.

The following information is needed to implement this technology:

- Type and homogenity of soils.
- Types of contaminants present.
- Dielectric properties of the soil matrix.
- The size of the area requiring treatment.
- Accessibility of the soil and the site.

3.4.2.4 Advantages of Radio Frequency Heating

The advantages of using this technology for remediation of hazardous waste sites are as follows:

- It offers a potentially high level of treatment.
- No other treatments are necessary if the contamination consists solely of volatile and semivolatile organics.

- It is economically feasible if soil consists primarily of sand and loams.
- It provides permanent remediation.

3.4.2.5 Disadvantages of Radio Frequency Heating

This technology has the following disadvantages:

- Has limitations related to various soil types and contaminants.
- Could be difficult to apply.
- Does not remediate nonvolatile organics, metals, or other inorganic contaminants.
- Must be supplemented with other treatment methods if nonvolatile contaminants are present.
- Very deep contamination would require more costly solutions.

3.4.3 Soil Cooling

Soil cooling is a technique for decreasing soil temperatures so as to reduce the vapor pressure of volatile constituents and thus their volatilization rates. One way to lower soil temperature is to apply cooling agents to the soil surface. Greer and Gross (1980) found solid carbon dioxide (dry ice) to be more effective than liquid carbon dioxide, liquid nitrogen, or ice in reducing ethyl ether vaporization from a liquid pool. Ethyl ether vapor concentrations were reduced from 8300 to 96 ppm by the addition of dry ice. The dry ice resulted in a liquid pool temperature of -85°C for 80 minutes at an application rate of 95 kg/m^3. Liquid nitrogen produced -120°C temperatures, but 1025 kg was required to reduce atmospheric concentrations from 93,000 to 116 ppm. Also, liquid nitrogen was more difficult to work with than was dry ice. Because of the effectiveness of solid carbon dioxide and the minimal risks it poses for response personnel during its application, it was the cooling agent of choice (Greer and Gross 1980).

Ground freezing is another means of immobilizing contaminants. Ground freezing involves injecting a cooling agent (e.g., ethylene glycol brine or liquid nitrogen) into pipes located within the soil matrix, which cools the soil to far below the freezing point of water (0°C) (Iskandar and Jenkins 1985). Artificial ground freezing is typically accomplished by the Poetsch method (Sullivan et al. 1984), which entails using uniformly spaced black-iron pipes within soils contaminated by volatiles. The coolant is injected and withdrawn in an open loop within each pipe to provide continuous recycling. Ground freezing to separate contaminants from water in a soil system is discussed in Section 3.5.3.

Sullivan et al. (1984) have determined that liquid nitrogen is the best coolant for quickly freezing contaminated soils. This fast freezing immobilizes volatile chemicals as the soil water (containing contaminants) freezes in situ.

This technology is apparently most suitable for immobilizing volatile organics at uncontrolled hazardous waste sites. The potential level of treatment is high; however, how effective the technology is depends on the degree of temperature reduction possible. Cooling agents are more effective than soil modifications, but cost may make their use impractical.

Cooling agents may be applied to the soil surface or circulated in a piping system below the surface. The soil characteristics and accessibility of the site determine the ease of application of this technology.

3.4.3.1 Status of the Technology

This technology is currently in the laboratory- and bench-scale stage. A literature search produced no reports indicating soil cooling or ground freezing had been demonstrated for soil vapor mitigation. Experimentation has been limited to certain types of contaminants. Laboratory studies of this technology have dealt specifically with liquid volatile organic compounds.

3.4.3.2 Secondary Impacts

Low temperatures may decrease or inhibit microbial activity. Extremely low temperatures may severely decrease microbial numbers or activity.

3.4.3.3 Equipment, Exogenous Reagents, and Information Required

Equipment requirements include machinery for creating vertical drill holes, piping, and recycling equipment. Cooling agents are the only exogenous reagents involved.

The following information is necessary for successful application of this technology:

- Characterization and concentration of wastes, particularly organics, at the site.
- Volatility of organic constituents (vapor pressure, Henry's law constant, air/water partition coefficient, solubility, and especially their dependence on temperature).
- Sorption of organics in soil (K_{oc}).
- Depth, profile, and areal distribution of contamination.
- Soil moisture.
- Effectiveness of cooling agents.
- Accessibility of soil and site.

3.4.3.4 Advantages of Soil Cooling

The primary advantage of applying this technology in situ is that no additional contamination (or chemicals for treatment purposes) would be added to the contaminated site, which precludes the need to recover such contaminants or additives.

3.4.3.5 Disadvantages of Soil Cooling

This technology has several inherent disadvantages.

- It is essentially a temporary remediation method, as the contaminants are bound only by the frozen water in the soil.
- It provides no degradation or removal of contaminants from hazardous waste sites.
- Although this technology has been shown to be effective against the migration of volatile organics, its effects on other types of contaminants (e.g., nonvolatile organics, metals, acids) have not been demonstrated.
- The use of cooling and freezing agents would not be reliable for large areas or for long periods of time.

3.5 Chemical and Physical Separation Techniques

Chemical contaminants can be removed from soil particles by physical and chemical means. This subsection discusses three such techniques: 1) permeable barriers; 2) electrokinetics; and 3) ground freezing. (Although permeable barriers are not directly used for soil treatment, the technology is an important in situ method for treating hazarous waste landfill leachate, which is why it is presented here.)

3.5.1 Permeable Barriers

Migration of leachate from hazardous waste deposits (i.e., landfills) presents a significant obstacle in attempts to remediate hazardous waste sites. Permeable barriers, which may be used to retain contamination within site boundaries, represent a potentially effective method of in situ treatment. The technology incorporates the use of readily available materials to adsorb contaminants from ground water as the contaminated plume migrates through the permeable barrier unit.

Permeable barriers may be used effectively to remove contaminants from leachate and to allow the treated leachate to migrate away from the contaminated source. There are several chemical and physical means of remediating hazardous waste sites by removal of contaminants from the leachate. Permeable barriers typically incorporate precipitation, physical and chemical adsorption, ion exchange, and filtration.

Commonly available and relatively inexpensive materials may be used to construct permeable barriers around hazardous waste sites. An example is activated carbon, which is widely used and is a strong sorbent for certain classes of chemicals. It is especially effective for removal of hydrophobic, high-molecular-weight organic compounds from liquid waste.

Activated carbon has been used to reduce the phytotoxicity and the crops' uptake of pesticides from the soil (Ahrens and Kring 1968, Anderson 1968, Lichtenstein et al. 1968, Coffey and Warren 1969, Gupta 1976, Weber and Mrozek 1979, Strek et al. 1981). For pesticide chemicals, activated carbon proved to be more effective on nonionic compounds; however, desorption may be significant.

Park (1986) has conducted bench-scale studies to quantify the remedial capabilities of materiasl such as coal, limestone, fly ash, and soils containing clay. Combinations of these materials in various sequences were tested to determine the optimum treatment barrier configuration. Because no individual material has the capacity to remove all the contaminants found at many hazardous waste sites, combinations of layers of materials possessing the qualities needed to retain the various contaminants at waste sites are needed. The bench-scale experiment was conducted to determine retentive capabilities of these materials and to evaluate the optimum layer depth and order of several common adsorptive materials.

Park (1986) used two connected units, each possessing six columns with a surface area of 412 cm^2. Each of these columns was packed to a depth of 36 cm with various combinations of soils, limestone, fly ash, and coal. The four materials used in the bench-scale analysis were chosen because they were locally available, which would be a cost-minimizing attribute for such materials at hazardous waste sites. A simulated hazardous waste leachate consisting of municipal landfill leachate spiked with phenol and dichlorobenzene was developed. During subsequent runs the simulated leachate consisted of various organic compounds listed in Table 21.

Table 21. Priority Pollutants Utilized in Permeable Barriers Experiment.*

Pollutant	Actual concentration, µg/liter
Bis(2-ethylhexyl)phthalate	163
Di-n-butyl phthalate	128
1,4-Dichlorobenzene	192
2,4-Dichlorophenol	109
Ethylbenzene	261
Fluoranthene	129
Isophorone	120
Pentachlorophenol†	136
Phenanthrene†	
Phenol	115
Pyrene	135
Naphthalene	137

* Source: Park 1986

† These two compounds could not be distinguished in the analytical procedure .

The simulated hazardous waste leachate was run through each of the columns packed with adsorptive materials. The order of the materials placed into each of the 12 columns is shown in Figure 11. The thinnest layers were 6 cm thick, and the intermediate and thickest layers were 10 cm and 20 cm, respectively. Two of the columns were dedicated to fly ash and coal only, because these two materials were expected to exhibit the greatest adsorptive capacity (Park 1986).

Effluent and interfacial samples were collected daily and analyzed for total organic carbon (TOC) content. As the simulated hazardous waste leachate passed through the columns, constituents of the leachate mixture were retained on the various components of the permeable barrier columns. Instead each individual retentive action (e.g., adsorption, ion exchange, precipitation, filtering, and chemical bonding) being measured, the cumulative effect of all of these mechanisms was measured to quantify the retentive capabilities of the permeable materials.

The results of the bench-scale study showed that coal retained more organics than did the other materials. Limestone retained very little TOC in both runs, which indicates its usefulness in treatment of organic-contaminated ground water may be limited. Table 22 lists the results for each of the permeable flow columns in Run No. 1 (leachate spiked with phenol/dichlorobenzene). Table 23 presents the results of the bench-scale study for the simulated leachate used in Run No. 2 (various organic compounds).

Figure 11. Schematic of permeable barrier bench-scale design.

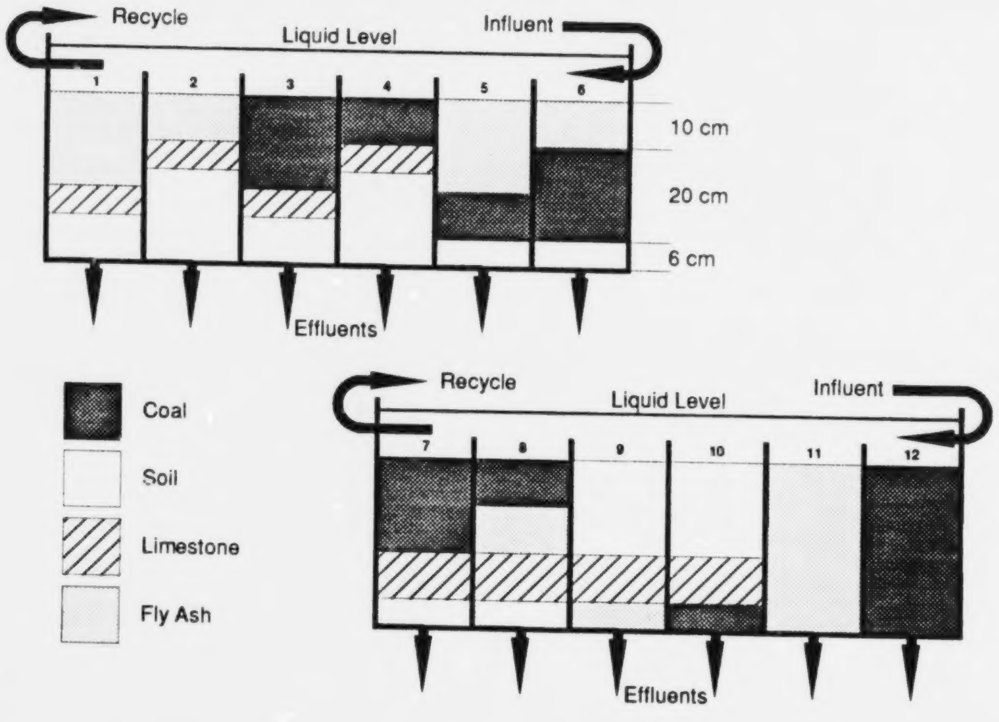


Table 22. Run No. 1 Column Performance

Column	Total flow, liter	Total TOC retained, mg	Days to 50% break through	Linear velocity, cm/day	Permeability, cm/day	Overall ranking
1	7.18	6337	16	19.3	0.78	8
2	6.66	7839	18	17.2	0.73	6
3	6.79	5709	9	10.2	0.96	11
4	3.93	5247	19	7.5	0.41	10
5	8.95	7299	11	18.8	0.98	4
6	7.74	6103	12	12.4	0.85	9
7	6.47	5177	7	9.2	0.91	12
8	9.22	10493	11	21.4	1.01	2
9	6.21	6567	12	27.8	0.68	7
10	9.23	11683	18	23.5	0.95	1
11	8.08	7900	19	9.4	0.84	5
12	8.92	12274	7	22.2	0.97	3

*Source: Park 1986

Table 23. Run No. 2 Column Performance*

Column	Total flow, liter	Total TOC retained, mg	Days to 50% break through	Linear velocity, cm/day	Permeability, cm/day	Overall ranking
1	15.86	4448	26	34.5	0.84	5
2	12.38	3857	39	21.7	0.52	9
3	25.78	7064	30	13.8	1.12	3
4	11.86	4310	47	8.8	0.50	8
5	23.99	6146	16	60.5	1.47	2
6	24.02	7525	37	41.2	1.01	1
7	26.12	6810	19	14.8	1.10	7
8	28.40	7006	20	16.0	1.19	4
9	14.35	3796	13	23.3	1.36	13
10	16.12	3911	14	25.9	1.00	12
11	17.00	4374	28	31.1	0.77	6
12	29.44	6533	15	8.2	1.23	10

*Source: Park 1986

Park (1986) developed three conceptual designs for use in the treatment of contaminated ground water: 1) a boundary treatment barrier, 2) a flushable barrier, and 3) a modular treatment system. Each design uses the most appropriate (based on test results) ordering of the permeable materials studied. Coal is used as the primary retaining material. Fly ash is used to moderate leachate flow and to reduce channeling into the coal. Limestone is used to adjust the pH after the leachate contacts with the layer of coal.

Three scenarios are described briefly (Park 1986):

- The boundary treatment barrier is designed to intercept the contaminated ground water from a site with a vertical wall of permeable materials for a given length of time.
- The flushable barrier is designed to make use of the ability of fly ash to elute all the organics retained when flushed with $CaSO_4$. After flushing, the fly ash will remain in place and be reused. Limestone will serve to precipitate cations and adjust pH.

- The modular treatment system is used when it is desirable to remove and properly dispose of the spent permeable materials. The rationale behind this design is to use the most appropriate orderings of permeable materials in modular, series-operated systems to allow easy replacement of spent treatment materials.

3.5.1.1 Status of the Technology

This technology is currently in the bench- and pilot-scale stage. It has not been tested at uncontrolled hazardous waste sites.

3.5.1.2 Secondary Impacts

The use of this technology requires that a treatment trench be constructed such that the permeable barrier may be installed. Also, the permeable barrier may become clogged with particulate matter and alter the rate of ground-water flow.

3.5.1.3 Equipment, Exogenous Reagents, and Information Required

No special equipment is required for implementing this technology; however, a backhoe may be necessary to construct the treatment trench for installing the permeable barrier. Permeable materials such as coal, fly ash, limestone, and activated carbon are required. Materials for installing drainage systems may be necessary. Information needed to implement this technology includes:

- Areal extent of contamination.
- Direction and rate of ground-water flow.
- Vertical location of ground-water table (and the extent of seasonal fluctuations of the ground-water table).
- Local availability of permeable retentive materials.
- Type(s) of contamination present.

3.5.1.4 Advantages of Permeable Barriers

This technology offers the following advantages:

- Use of commonly available retentive materials.
- Removal of contamination (i.e., permanent treatment).

3.5.1.5 Disadvantages of Permeable Barriers

Disadvantages of using this technology are as follows:

- Potentially low treatment levels.
- Possible migration of contamination offsite (if retentive capacities of permeable materials are reduced by flow rates or variable contaminant concentrations).
- Need to treat or dispose of contaminated permeable materials.

3.5.2 Electrokinetics

Electrokinetics has been used for more than 50 years to dewater and stabilize soils (Spangler and Hardy 1973). It is hoped that it will produce similar results at hazardous waste sites.

An electrokinetic phenomenon referred to as electroosmosis occurs when a liquid migrates through a charged porous medium under the influence of a charged electrical field (Murdoch et al. 1988). The charged medium is usually some kind of clay, sand, or other mineral particles that characteristically carry a negative surface charge.

When the charged particles come into contact with water molecules, they attract positive ions, which effectively neutralize their negative surface charge. As a result, cations predominate in the layer of water next to the surfaces of the particles and create what is referred to as a "diffuse double layer."

If an electric field is applied to the saturated medium through anodes, cations bound in the diffuse double layer will migrate toward the negatively charged cathode. The viscous drag of water molecules due to the migration of the cations produces a net flow of water toward the cathode. The application of an electrical field induces the water to flow (Murdoch et al. 1988).

The chemical reaction inherent in electroosmosis produces a cathodic reaction, specifically the electrolysis of water. Subsequently, hydrogen is reduced to form hydrogen gas. The removal of hydrogen ions from the soil solution increases the soil pH, and soils have been known to have pH values in excess of 13 (Murdoch et al. 1988).

If the electrolysis is continued, concentration gradients in the soil solution are established between the cathode and anode (Murdoch et al. 1988). The concentration gradients cause diffusion from areas of low concentrations to areas of high concentration. This diffusion may be in the same direction as the ion conductance transport, or it may occur in the opposite direction (Murdoch et al. 1988)

The Helmholtz-Smoluchowski model is a widely used theoretical description of electrokinetics. The basis of this model is similar to that of Darcy's law, which uses solutions to groundwater flow problems to estimate electroosmotic flow rates (Murdoch et al. 1988). The major difference between the Helmholtz-Smoluchowski model and Darcy's law is the independence of K_e (the electroosmotic permeability constant) from hydraulic conductivity. Soil porosity and the zeta potential of the capillary walls apparently exert the most influence on electroosmotic potential (Murdoch et al. 1988).

Ionic metal species that are subject to ionic reaction and migrate in the soil system appear to be the types of contaminants that can be effectively treated with electrokinetics.

The potential treatment levels achievable with electrokinetics range from low to medium, depending on soil and site characteristics and the waste type(s) present. This technology may be difficult to demonstrate in the field. The fact that it is easy to apply could make the electrical power requirements excessive for the level of cleanup achieved in large areas of contamination.

3.5.2.1 Status of the Technology

Horng and Banerjee (1987) investigated the use of electrokinetics for the remediation of a hazardous waste site (the United Chrome Superfund site near Corvallis, Oregon). The area selected for testing consisted of approximately 0.6 hectare of level ground, which was enough for the electrokinetics experimentation. The investigators determined that this areal extent, a nearly static ground-water regime, and saturated moderately permeable soils at a shallow depth are favorable conditions for applying electrokinetics as a remedial technology.

Contamination at the United Chrome site includes inorganics that exist in the soil system as ions. The most important of the contaminants, hexavalent chromium (Cr VI), exists primarily in the anionic forms CrO_2^{-4}, $HCrO_4^-$, or $Cr_2O_7^{2-}$, depending on the concentration of the individual chromium ions and the pH of the soil system. The removal of the toxic forms of chromium was the goal of remedial action testing at this site. Because chromates, which do not react with soils, are a major ionic constituent in the soil, transportation of the ions through the soil matrix at this site was achievable with high-efficiency and relatively low power consumption (Horng and Banerjee1987).

After conducting several tests on the soils at the United Chrome site, Horng and Banerjee (1987) concluded that a treatment combination of hydraulic leaching and electrokinetics can accelerate chromium removal compared with the use of hydraulic leaching alone. They also concluded that the possible methods of action involved in the use of electrokinetics are dispersion due to hydraulic flow, ion migration, water electrolysis, adsorption/desorption, and chromium reduction resulting from the applied electrical field.

3.5.2.2 Secondary Impacts

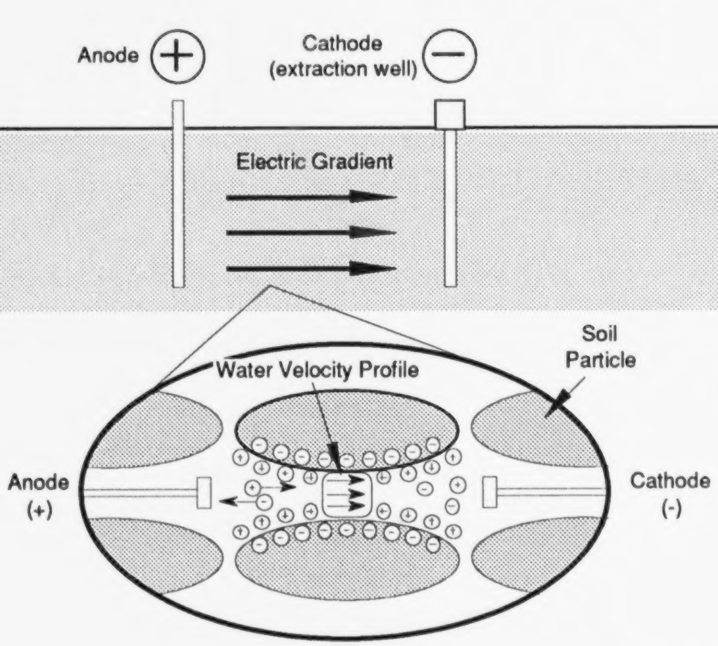
This technology may raise the soil pH to levels that result in the mobilization of metallic contaminants. The high pH levels could also inhibit or destroy the microbial population present within the soil matrix.

3.5.2.3 Equipment, Exogenous Reagents, and Information Required

The schematic presented in Figure 12 shows the equipment used by Horng and Banerjee (1987) . No exogenous reagents are required for this technology. The following information is needed to implement this technology:

- Hydraulic conductivity of the contaminated soil.
- Areal extent of contamination.
- Ground-water flow rates.
- Ground-water depth characteristics, including seasonal changes in the depth.
- Permeability of soils.

Figure 12. Diagram of a typical electrokinetic operation.


Anode
Cathode
(extraction well)
Electric Gradient
Soil
Particle
Water Velocity Profile
Anode
(+)
Cathode
(-)

3.5.2.4 Advantages of Electrokinetics

This technology offers the following advantages:

- The remediation of contaminated sites is permanent.
- The contaminated soil solution is easily extracted from the point of collection.

3.5.2.5 Disadvantages of Electrokinetics

This technology has the following disadvantages:

- The technology is confined to sites contaminated with metals.
- Electrical power requirements could be excessive; thus the technology might not be cost-effective.
- The effects on the soil matrix itself are unknown.
- Further treatments would be required for sites contaminated with organics or other waste types.
- Precipitation of salts and secondary minerals could decrease the effectiveness of this technology.

3.5.3 Ground Freezing

Laboratory studies have shown artificial ground freezing to be a potentially effective method of driving volatile organic contaminants from soil matrices (Iskandar et al. 1986). Contaminants can be removed from soils by using the differences in the physical and chemical properties of the water and contaminants within the soil. When the temperature of soil is gradually lowered below 0°C, ice nucleation starts in the soil water and ions are rejected. As the dissolved chemicals in the soil solution are excluded from the ice, they become more concentrated in the remaining liquid. As the temperature drops further, the amount of ice becomes larger and the amount of unfrozen water decreases (Iskandar and Houthoofd 1985, Iskandar and Jenkins 1985). The concentrated solution is pushed ahead of the ice lense in a desired direction, as determined by the location of the cooling system. This large bulb of concentrated contaminated soil may then be treated separately without treating the entire soil mass.

If a situation requires the contaminants to be immobilized, the temperature should be dropped rapidly rather than gradually. In this case, the ions and salts are entrapped between the ice particles and the separation process will not be complete (Iskandar and Houthoofd 1985). This concept was discussed in Section 3.4.3.

Iskandar et al. (1986) used 80-cm high plexiglass columns filled with a dredged sludge saturated with a solution modified with four metals (Cd, Zn, Cu, and Ni) and four volatile organics (chloroform, benzene, toluene, and tetrachloroethylene). Six separate treatments (and two controls) were compared; one column was used for each treatment. During each treatment, soils were gradually frozen from the bottom up. Thermocouples were used to measure soil temperatures at various depths. Soil temperatures ranged from -1.8°C to -16.0°C, and frost penetration rates varied from 15 to 50 cm per day. After each episode of freezing, the soil columns were permitted to thaw and leachate was allowed to drain from the soil columns. The leachate was analyzed for the metals and volatile organics used to spike the soils.

Using such freeze/thaw cycles reduced the volumes of the soil columns. The consolidation of the soils resulted from the physical effects of the freeze/thaw cycles. Iskandar et al. (1986) concluded that freezing and thawing saturated sediments can decrease the amount of time necessary to remove water relative to natural processes. The rate of water migration through the treated columns was enhanced to approximately 3 times the magnitude of natural drainage because of the formation of aggregates and cracks in the soil matrix as a result of repeated freeze/thaw cycles.

The effects of freezing/thawing cycles on the recovery of the volatile organics used to spike the soils was inconsistent (see Table 24). The one- and three-cycle treatments had similar effects on the amount of volatile organics recovered from the soil and leachate. The two- and five-cycle treatments, however, had a much lower percentage recovery compared with the other treatments. The volatile organics were believed to have volatilized from the experimental apparatus, which reduced the recovery rate for the volatile compounds. Apparently, increased numbers of freeze/thaw cycles had little effect on the amount of volatile organics recovered from the columns, even though the cycles enhanced the rate of volatilization.

Table 24. The Effects of Freeze/Thaw Cycles on Contaminant Recovery*

Column number	Freeze/thaw cycles	Time, days	% Volume reduction	Total VOC recovery, %	Average metals recovery, %
1 (control)	0 (frozen)	50	34	80	97
2 (control)	0 (unfrozen)	125	36	36	84
3	1	12	28	ND[a]	94
4	1	70	34	62	94
5	2	22	37	33[b]	91
6	3	27	36	70	ND
7	3	41	37	ND	ND
8	5	50	35	16	ND

*Source: Iskandar et al. 1986.
[a] ND - Not determined.
[b] Does not include recovery of toluene (not determined).

Metal concentrations were also analyzed in the leachate and column sections. Unlike the reduction in concentrations of volatile organics, some metals concentrations increased in the treated columns as a result of the volume reduction and the high retention of metals in the sediment. Therefore, as the amount of metals present (on a mass basis) remains fairly constant (freezing from the bottom up prevented metal leaching) and volume is reduced, metals concentrations increase.

Artificial ground freezing may enhance water percolation through soils as a result of aggregate and channel formation (which could be used in conjunction with delivery/recovery systems). It may also provide a barrier to the input of volatile organics and metals entering the ground water when soils are frozen from the bottom to top, and enhance the ability to remove volatile organics from contaminated soils.

3.5.3.1 Status of the Technology

Artificial ground freezing is currently in the bench-scale stage. Ayorinde et al. (1989) have reported preliminary results from a laboratory study to evaluate the possibility of mobilizing different types of contaminants by freezing. Two types of contaminants were studied: explosives and volatile organic compounds (VOCs). Preliminary data indicate a certain degree of movement of both explosives and VOCs when the soil columns spiked with these contaminants were frozen unidirectionally from the bottom up. For given freezing rates, freeze-thaw cycles, soil types, and moisture contents, it appears that the ability to move any contaminant by freezing depends on the type and initial concentration of the contaminant, and the interaction of the soil and the contaminant (Ayorinde et al. 1989).

3.5.3.2 Secondary Impacts

Low temperatures may decrease or inhibit microbial activity. Extremely low temperatures may severely decrease microbial numbers or activity.

3.5.3.3 Equipment, Exogenous Reagents, and Information Required

Equipment requirements include machinery for creating vertical drill holes, piping, and recycling equipment. Cooling agents are the only exogenous reagents involved. The following information is necessary for successful application of this technology:

- Characterization and concentration of wastes, particularly organics, at the site.
- Volatility of organic constituents (vapor pressure, Henry's law constant, air/water partition coefficient, solubility, and especially their dependence on temperature).
- Sorption of organics in soil (Koc).
- Depth, profile, and areal distribution of contamination.
- Soil moisture.
- Effectiveness of cooling agents.
- Accessibility of soil and site.

3.5.3.4 Advantages of Ground Freezing

The advantages of ground freezing are as follows:

- No additional chemicals are added to the contaminated soils.
- The size of the area to be treated can be reduced by concentrating the contaminants in one location.
- Permeability of the soils increases.
- Contaminants can be separated from the soil mass.

3.5.3.5 Disadvantages of Ground Freezing

This technology has several inherent disadvantages:

- It concentrates metals in the soil and allows organic vapors to enter the air around the site.
- The use of cooling agents and piping systems to deliver freezing agents through the site may not be cost effective.
- The use of freezing agents to immobilize contaminants would not be reliable for large areas or for long time periods.

Section 4
Delivery and Recovery Systems

Delivery/recovery systems refer to technologies that either deliver remediating materials into environmental compartments or recover contaminating materials from these compartments. Delivery technologies generally involve the transport of remediating materials into soils or ground water. The delivered materials are usually liquids; however, newer technologies involve the delivery of solids, gases, and vapors as well. Recovery technologies generally remove contaminants from these same environmental compartments. This latter category includes technologies that expedite removals by altering the physical or chemical attributes of contaminants or pathways. Recovery technologies typically involve fluid flows driven by hydraulic gradients, thermal methods, or chemical reactions.

Delivery/recovery technologies have been used in hazardous waste site remediation for several years. Most of these technologies involve pumping ground water from recovery wells, treating it, and then reintroducing it at injection wells. Such "pump and treat" technologies vary in effectiveness with variations in site and contaminant properties. In addition, dense soil formations (with hydraulic conductivities of less than 10^{-4} cm/s) severely limit the application of recovery techniques to contaminated hazardous waste sites.

Other problems associated with the implementation of delivery and recovery systems at waste sites include the presence of contaminants with low solubilities; adsorption of contaminants onto clayey soils; the existence of fractured soils or rocks, which create pathways of high conductivity separated by a matrix block of low conductivity; and the absence of an underlying impermeable layer to preclude the possibility of delivered materials migrating into the ground water.

Delivery/recovery technologies include some of the technologies described in other sections of this document; for example, although vapor extraction is a recovery technique, it is described in the subsection dealing with the control of volatile materials. Table 25 lists other delivery/recovery technologies that are described elsewhere in this report.

Table 25. Delivery/Recovery Technologies Cross-Reference

Delivery/Recovery Technology	Included in this report under
Colloidal gas aphrons	Section 3.3
Vapor extraction	Section 3.4
Steam stripping	Section 3.4
Radio frequency heating	Section 3.4
Electrokinetics	Section 3.5
Ground freezing	Section 3.5

Discussed in this section are several delivery and recovery technologies (hydraulic fracturing, radial drilling, kerfing, and cyclic pumping) and technologies identified as recovery only (ultrasonic methods, jet slurrying, CO_2 injection, and hot brine injection).

4.1 Hydraulic Fracturing

Hydraulic fracturing, a technology widely used in the petroleum industry, stimulates the recovery of hydrocarbons from low-permeability reservoirs and enhances the delivery of fluids used to displace petroleum in sweeping operations (Murdoch et al. 1988). The technology involves the injection of a fluid (typically water) at pressures exceeding the confining pressures at the bottom of a borehole. This process generates a single fracture (either horizontal or vertical) that propagates away from the borehole. Sand is introduced into the formed fracture to hold it open and to create a highly permeable channel suitable for either the delivery of remediating materials or the recovery of contaminants.

Preliminary investigations consisting of theoretical calculations and comparative investigations on applications developed by the energy industry suggest that this technology can be used with soil and rock types commonly found at contaminated waste sites. Possible applications include increasing the efficiency of pump and treat systems, stimulating the extraction of vapor phases from dense soils, or forming a horizontal drain to capture leachate (Murdoch et al. 1988).

Murdoch (1989) conducted theoretical analyses of ground-water flow that indicated hydraulic fractures could significantly increase the yields of recovery wells. Immediately after the fracturing, the yields could increase tenfold or more. Over time the yield from a fractured well will diminish, but can eventually maintain a yield of two times that of an unfractured well.

Volumes of ground water extracted from contaminated aquifers can be estimated theoretically as a function of time (Murdoch et al. 1988). The recovered volume obtainable by using hydraulic fracturing at well sites also depends on the length, width, and conductivities of the fractures and the enveloping formation. Application of the theory to the expected values of the preceding variables indicates that the volume of water recovered from a well intersecting a hydraulic fracture could be an order of magnitude greater than the volume obtainable from an unfractured well.

Murdoch (1989) conducted a field test to evaluate the characteristics of fractured soils. Unlithified glacial till (hydraulic conductivity ranging from 1.5×10^{-6} to 1.9×10^{-7} cm/s) was fractured by injecting a mixture of water, sand, and chemicals (a gel and a dye) into 11 separate boreholes with depths ranging from 1.64 to 3.81 m.

The fractures formed by the process typically vented to the surface. The largest fracture covered 90 m^2 and extended 13.5 m from the borehole when it vented to the surface. A typical fracture covered approximately 20 m^2 and extended 5 to 8 m from the borehole. A maximum thickness of 1 cm of sand was observed in the fractures.

The following conclusions were drawn from the field test conducted at a contaminated site (Murdoch 1989):

- Hydraulic fractures can be created at shallow depths in glacial till. The fractures are elongated in plan and dip gently toward the parent borehole.
- Injection pressure can be used to determine the onset of hydraulic fracturing in till. Tilt meters can be used to monitor growth of hydraulic fractures at shallow depths. Electrical geophysical methods may be useful as monitoring tools.
- Equipment used to create hydraulic fractures at oil wells can be used to create hydraulic fractures at contaminated sites. Equipment designed for creating hydraulic fractures at shallow depths should perform better than that used by the oil industry.

4.2 Radial Well Drilling

Radial (horizontal) wells drilled outward from a central borehole may be used to enhance access to a contaminated soil system or ground-water aquifer. Multiple wells may be placed at the same or various levels within the same borehole. Potential applications of this technology include ground-water extraction and delivery of in situ remediating materials.

Initial applications of this technology involved drilling a central downward core sufficiently wide to allow a worker to descend into the borehole and to drill radially outward. Recent developments made by the petroleum industry have dramatically improved the method of drilling horizontal wells. This new system includes a jet nozzle fixed to 1.25-inch-diameter tubing (used to create the horizontal well) and a whipstock, which is placed at the bottom of the vertical borehole to redirect the jet nozzle and tubing horizontally into the formation (Dickinson et al. 1987). Radial wells are created by pumping high-velocity water out of the jet nozzle. The water for this process is supplied from the surface through steel tubing. This equipment cuts a borehole with a diameter several times larger than the tubing (Dickinson et al. 1987). In addition, static pressure on the inside of the nozzle results in a force that pulls the nozzle and attached tubing down the drill stem, through the whipstock, and into the radial well. This force is responsible for keeping the radial progressing in a straight line.

The whipstock is erected in a 24-inch-diameter cavity. This device consists of a series of slides and wheels that redirect the tubing from a vertical plane in the main borehole through a 90-degree bend to a horizontal plane. This redirection occurs within a 9- to 12-inch bend radius (Dickinson et al. 1987).

A wireline system has been developed to locate each radial produced by the jet nozzle. The wireline, which is quite flexible and thin, is run through the 1.25-inch tubing. The device logs the horizontal and vertical location and records the length of the radial (Dickinson et al. 1987).

For completion of the radial well, techniques have been developed that will electrochemically perforate and cut off the tubing within each radial, place a slotted liner within the perforated tube, and gravel-pack the tube. The gravel packing is accomplished in two separate steps: 1) gravel is pumped out of the end of the 1.25-inch tube and forced toward the borehole, and 2) gravel is forced from the borehole into the radial well (Murdoch et al. 1988).

In the petroleum industry this technology has been applied to both consolidated rock and unconsolidated soils. As can be expected, the rate of placement in rock is much less than the rate of placement in soils. Murdoch et al. (1988) report that drilling rates in unconsolidated materials range from 5 to 120 feet per minute. Rates in consolidated, hard, and homogeneous basalt range from 0.10 to 0.50 foot per minute.

Radial wells applied to hazardous waste sites can be positioned in both saturated and unsaturated media and can facilitate the remediation of contaminated sites by increasing the available delivery/recovery routes for delivering remediating materials or recovering contaminated ground water. The technology, although not fully demonstrated at hazardous waste sites, is the focus of current research and is being refined for that purpose.

4.3 Ultrasonic Methods

Ultrasonic methods (ultrasonic vibrations) can be used to increase the efficiency of recovery wells. Extrapolations from current applications of ultrasonic methods can be used to describe the mode of action at sites requiring remediation. At least three potential applications to hazardous waste sites have been identified: 1) the dispersion or disaggregation of clay particles during cleaning of pores or well screens by enhancing the removal of chemicals adhered to solid particles (which could improve recovery efficiency), 2) the sterilization of wells, and 3) the elimination of microbes that clog pore spaces. This technology could eliminate the need for antibacterial agents in the cleaning of wells used in bioreclamation.

Soil scientists have used this technology extensively to disperse clay and silt particles. Ultrasonic methods have also proved to be effective for removing mineral films and clay aggregates from sand grains (Busacca et al. 1984).

Laboratory tests involving the use of ultrasonic methods have shown that they often reduce the time required to extract humic acids (Ramunni and Palmieri 1985), to leach various metallic ions from soils (Tamari et al. 1982), and to clean MoS_2 from steel surfaces (Bertrand and Vuleasovich 1977).

Ultrasonic methods may be used to increase recovery volumes from wells clogged with clay particles or microorganisms and to separate contaminants from clay particles near well sites.

Murdoch et al. (1988) describe a laboratory-scale test of an ultrasonic method. An experiment was conducted to determine the effect of ultrasonic vibrations on a mixture of sand and clay in a rigid-wall permeameter. Several falling-head permeability tests conducted on the mixture showed consistent results of 3.8×10^{-4} cm/s for the hydraulic conductivity of the sample. The permeameter was then placed in an ultrasonic cleaning chamber used to clean samples in the laboratory. A falling-head permeability test was conducted while the cleaning apparatus was turned on for 30 seconds. The hydraulic conductivity abruptly increased one order of magnitude to 1.8×10^{-3} cm/s, and the effluent changed from clear water to a turbid mixture of clay and water. The results show that this method effectively dislodged clay particles and caused them to be removed by flow through the permeameter.

4.4 Kerfing

Kerfing (or borehole notching) is currently used to produce a slot either perpendicular or parallel to the axis of a previously drilled borehole. This technology has aroused interest as a possible method for preventing the migration of pollutants from hazardous waste sites; however, kerfing may also have applications as a recovery technique (Murdoch et al. 1988).

Kerfing was developed in the United States and Europe; however, Huck et al. (1980) indicate it was first applied in Japan. Kerfing is used primarily as a method of placing barriers of low permeability beneath hazardous waste sites to intercept leachate and to prevent further ground-water contamination (Huck et al. 1980).

This technique uses a high-pressure water jet and and an abrasive material (e.g., sand) to cut a slit in the wall of a borehole. The high-pressure water jet is placed in an existing borehole, where it is rotated to cut a disk-shaped cavity, moved along the axis of the hole to create an axial slit, or kept in place to cut a cylindrical hole. The water jet advances the kerf at a rate of several centimeters per second, and the final slit or hole is 1 to 3 m long. The slot created is subsequently filled with a permeable material to create a drain, an impermeable material to create a barrier, or a remediating material to facilitate cleanup (Huck et al. 1980).

Two methods are currently used to construct impermeable barriers with this technology. One method involves implacing a floor by kerfing a series of disk-shaped cavities and filling them with bentonite slurry. This method has been referred to as "pancake slurry jetting" (Murdoch et al. 1988). The other method uses this technique to initiate hydraulic fractures. Two adjacent boreholes are concurrently pressurized with a fracturing fluid (a cement/grout mixture), and fractures are propagated outward from the kerfs. As the fractures approach each other, the stresses at their tips tend to cause the fractures to intersect (Huck et al 1980). Continued injection of the grout forms a continuous impermeable layer. This method was used to form an impermeable barrier at a Whitehouse, Florida, site (Brunning 1987).

Kerfing may also be suitable as a technique for improving recovery processes. A potential method of improving recovery would be to fill the kerf with a highly permeable material (much as a hydraulic fracture is filled with sand), which would improve the yield of a recovery well.

As a recovery technique, kerfing appears to be most applicable to materials of low permeability, such as clay, silt, or rock, where most contaminants would be immobile (Murdoch et al. 1988). Using kerfing to increase the rate of recovery from recovery wells is undocumented. The rate could be expected to increase by a factor of 2 to 10 compared with the rate before fracturing (Murdoch et al. 1988).

Kerfing is widely used in the petroleum industry (where it is referred to as borehole notching) to initiate hydraulic fractures. Some oil field service companies provide borehole notching services.

4.5 Jet-induced Slurry Method

The jet-induced slurry method is a mining industry technique used to excavate an ore formation by fragmenting the subsurface ores with a high-velocity hydraulic jet and then pumping the slurry to the surface through a borehole (Murdoch et al. 1988). This technology enables solid ores to be recovered from the the subsurface at any depth without presenting the disposal problems of overburden.

The use of high-pressure water jets to slurry ore-bearing rock is not a new technique; it has been used for more that 100 years to mine placer gold and gilsonite at the ground surface. The application of this technology to subsurface formations, however, has only occurred within the past few years (Kasper et al. 1979).

The jet-induced slurry method (called "in situ borehole slurry mining" by the mining industry) is facilitated by drilling an 18-inch borehole to roughly 6 feet below the bottom horizon of an ore-bearing formation and installing a sump pump at the bottom of the borehole, below the hydraulic jet. The jet slurries the rock in the ore zone and the slurry flows to the sump, where it is pumped to the surface for processing. The tailings from the processing are used to backfill the cavity left by the excavation (Kasper et al. 1979).

Solid materials may be removed up to 75 feet away from the borehole, depending on the properties of the ore body and the jet system. Typically, the jet is rotated through an arc of about 300 degrees, which leaves a portion of the ore body unmined for roof support (Murdoch et al. 1988). For complete mining of an ore formation, wells are aligned so that adjacent wells slurry and remove the roof supports from previous wells.

Although no documented applications of the jet-induced slurry method for remediation of hazardous waste sites were found, this technique should be applicable to any soil or rock formation that could be fragmented by a hydraulic jet. Lithified sediments, including pebble phosphate deposits in Florida and North Carolina and uranium-bearing sandstones in Wyoming and Texas, have all been successfully mined with this technology (Kasper et al. 1979). Ore bodies located both above and below the water table have been mined by the jet-induced slurry method, but fewer complications arise during the mining of ore bodies above the water table (Kasper et al. 1979).

4.6 Carbon Dioxide Injection

Implementation of this technology in the petroleum industry involves injecting carbon dioxide (CO_2) into oil-bearing rock formations to maintain pressure and to displace the oil. The two principal mechanisms for mobilizing the oil by carbon dioxide injection are the reduction of the oil viscosity upon solution of the gas into the oil and an increase in the volume of the reservoir (Holm 1987; Donaldsen et al. 1985; Morrow and Heller 1985).

Use of this technology for the recovery of ground-water contaminants probably would be limited to applications where CO_2 is either dissolved in water or contained in aphrons. In either case, the injection of carbon dioxide could decrease the viscosity and increase the recovery of hydrocarbons (Murdoch et al. 1988). It has been reported that injecting CO_2 at high pressures (approximately 1200 psi) increased its solubility in oil and dramatically reduced the viscosity of the oil (Grogan and Pinczewski 1987; Holm 1987, Collins and Wright 1985; Latil 1980). The feasibility of applying this technique to a site where contamination is near the surface is questionable. The pressure exerted by the injection stream may be sufficient to displace (with great force) the soil overburden.

Reduction of the viscosity of the oil results in two phenomena that should increase recovery. A decrease in viscosity results in an increase in mobility and thereby decreases the head gradient required to sustain flow. A decrease in the difference in the viscosities of the oil and the fluid used to displace it tends to minimize the formation of viscous instabilities or fingers (Holm 1987).

The most effective method for introducing CO_2 involves following a CO_2 slug with alternating water and CO_2 injections. Other methods involve the injection of water saturated with CO_2 and the application of high-pressure injections of the gas itself (Holm 1987).

Successful CO_2 injection programs have been implemented in limestones and dolomites with 10 to 15 percent porosity and 5 to 25 mD permeability (Pittaway et al. 1987; Albright 1986, Pittaway et al. 1985; Ader and Stein 1984). Homogeneous permeability is preferred, but not necessary (Collins and Wright 1985).

The volumetric ratio of the CO_2 injected to the oil recovered ranges from 0.1 to several hundred (Williamson et al. 1986; Desch et al. 1984; Ehrlich et al. 1984; Bolling 1985; Boyer 1985). Reservoirs depleted to less than 10 percent of the original oil in place have overall injection-to-recovery ratios of 0.09 to 0.1 (Williamson et al. 1986; Desch et al. 1984).

Carbon dioxide flooding is one of the major enhanced oil-recovery processes in the United States (Holm 1987). It has been applied successfully in many large and small oil reservoirs around the world. Sophisticated computer simulations of specific reservoirs permit oil companies to estimate the optimal rates and pressures for gas injection and the corresponding rates of oil recovery. Laboratory studies have concentrated primarily on substitute gases and alternate gas-fluid or gas-gas injection mechanisms (Holm 1987).

4.7 Hot Brine Injection

Natural gas deposits typically occur as liquids or solids at existing pressures in many reservoirs. Because extraction of these liquid or solid deposits is more difficult than extraction of the gas in vapor phase, petroleum engineers have developed methods for converting the gas from the solid or liquid phase to the vapor phase (Kamath and Godbole 1987).

The hot brine injection method for recovering natural gas hydrates appears to be limited to depths greater than 150 m because the hydrate equilibrium curves indicate lower dissociation temperatures are needed than the ambient earth temperatures that occur at shallow depths (Kamath and Godbole 1987). The dissociation temperature could be reduced through the artificial increase of salinity of the pore solution, however, to facilitate the recovery of contaminating chemicals with a dissociation temperature exceeding the temperature at shallow depths. For this method to be used successfully, the dissociation temperature of the contaminant to be recovered must have a salinity dependence.

At depths of approximately 150 to 1000 meters, the temperature of hydrate dissociation from a solution with no salinity exceeds the ambient temperature of the surrounding earth by almost 10°C (Kamath and Godbole 1987). Increasing the salinity of the pore solution to 15 weight percent reduces the temperature of hydrate dissociation by about 11°C. The relationship between salinity and dissociation temperature reduction is approximately linear within the range of 0 to15 weight percent salinity (Kamath and Godbole 1987).

The amount of thermal energy required to dissociate gas hydrates into a pure gas vapor phase and liquid water decreases as dissociation temperatures decline. Increasing the salinity of the pore solution from 0 to 15 weight percent reduces the energy of hydrate dissociation by nearly 8 percent (Kamath and Godbole 1987).

The principal mechanism of hot brine injection is the reduction in dissociation temperature resulting from an increase in salinity. Reducing the dissociation temperature decreases the thermal energy required during recovery .

A minimum porosity of 15 percent is required for effective use of this technology. At lower porosities, gas production declines rapidly. At porosities greater than 15 percent, gas production does not change significantly. Because hydrate dissociation energy is directly proportional to porosity, excessive porosity (greater that about 50 percent) is also undesirable (Kamath and Godbole 1987).

A minimum thickness of 7 m at the hydrate zone is required for effective use of this technology. This thickness minimizes heat loss to surrounding rock or earth, especially to overlying material. The energy efficiency of this technology increases significantly with increases in the thickness of the hydrate zone up to about 100 m. Beyond 100 m, the increase in energy efficiency is small (Kamath and Godbole 1987).

Salt precipitation may cause pore occlusion over extended periods of time, which would hamper gas recovery (Murdoch et al. 1988). The optimal temperature range is between 120° and 200°C. The use of very high brine temperatures may cause severe heat loss and reduce the energy efficiency ratio. When very low injection temperatures are used, high brine input rates are required to increase gas production (Kamath and Godbole 1987).

Theoretically, the efficiency of gas production via hot brine injection ranges from 150 to 200 standard cubic meters of gas extracted per cubic meter of hot brine injected. In general, the higher the salinity of the injected brine is the higher the rate of return of extracted gas.

The ratio of heat injected to the heat value of the gas produced (the energy efficiency ratio) ranges from 5 to 11. It increases with porosity, reservoir layer thickness and burial depth, brine injection rate, salinity, and temperature (Kamath and Godbole 1987).

The proposed stimulation of contaminant removal by use of hot brine is based on the results of theoretical analyses. The technique has not yet been tested in the laboratory or field.

4.8 Cyclic Pumping

Cyclic pumping (both a delivery and recovery technique) varies the rates of either injection or extraction in an effort to minimize pumping costs . Optimizing pumping activities could conceivably reduce remediation costs at contaminated waste sites (Murdoch et al. 1988).

In typical pump and treat operations, the pumping rates are usually held constant, as opposed to a cyclic pumping operation, in which the rates are variable and the pumps are turned on during active cycles and turned off during rest cycles. Pumping in this manner (active and rest cycles) can be accomplished for either the injection of treating solutions or the extraction of contaminated ground water (Keely et al. 1987).

The purpose of a rest cycle is to permit sufficient time to elapse for diffusion between high-permeability channels (fractures or large pores) and the comparatively low-permeability blocks between them. Pumped treatment solutions diffuse from the pathways into the low-permeability areas, and contaminants diffuse from these areas to the high-permeability channels during a rest cycle. The active cycle of cyclic pumping is designed to deliver the necessary volume of reactants or to recover the necessary volume of reaction products (Keely et al. 1987).

Because no applications of cyclic pumping at contaminated hazardous waste sites are documented, no information on appropriate site conditions is available. It appears, however, that cyclic pumping would be most effective in soils composed of preferred high-permeability channels and low-permeability blocks.

The petroleum industry uses this technique to enhance oil recovery. Techniques include cyclic water flooding and steam stimulation (cyclic injection). Cyclic water flooding involves an injection of water to restore reservoir pressure, followed by an extended period of oil extraction. When production rates decline, water is again injected and the cycle is repeated (Aguilera 1980).

These techniques are designed to increase the efficiency of pump and treat systems by increasing the concentration of contaminants recovered (or reactants delivered) per volume of ground water (Murdoch et al. 1988). The diffusion that occurs during the rest cycle between the low-permeability blocks and the preferred high-permeability channels is the rate-limiting step in the cyclic pumping technique and may limit the use of this technology. The time required for a sufficient quantity of contaminants to diffuse into the channels may increase the time it takes for complete remediation of a site and thus render the technology economically infeasible.

This technology has been proposed for use at contaminated waste sites, and EPA is initiating research on this subject.

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Appendix A
Modification of Soil Properties

Introduction

Implementation of in situ treatment techniques for contaminated soils often involves the modification of soil properties. Biological degradation, for example, can be enhanced by the addition of nutrients, and immobilization of heavy metals may require adjustment of soil pH. Soil properties discussed in this section include

- Oxygen content
- Moisture content
- Nutrient content
- pH
- Temperature

This section emphasizes the mechanics of soil property modification, independent of the treatment technology. Table A-1 lists the technologies of Section 3, indicating which soil properties may require modification as a part of treatment.

Control of Oxygen Content

Oxygen content in surface soils can be increased primarily through the use of tillage equipment which breaks, mixes, and aerates the soil. Alternatively, oxygen content can be decreased by compaction or increased moisture content. Aeration of subsurface soils not accessible to tillage equipment can be accomplished using construction equipment, such as a backhoe, or using a well point injection system.

A variety of tilling equipment is available to aerate surface soils. Tilling equipment can also be used to mix wastes or reagents into the soil. Choice of equipment depends on the amount of soil disturbance or mixing desired, and on site characteristics such as the rockiness of the soil.

For some processes, such as anaerobic biological degradation, surface soil compaction may be desirable. By reducing pore sizes and restricting reaeration, anaerobic microsite frequency in the soil will increase. Compaction helps draw moisture to the soil surface. Thus, the problems of leaching that may occur if anaerobiosis were achieved by water addition would be lessened. If the compaction itself were not adequate to achieve the required degree of anaerobiosis, water could be added. Less water, however, should be required in a compacted soil than in an uncompacted soil; thereby minimizing the leaching potential. Volatilization may also be suppressed by surface soil compaction.

Aeration of soils deeper than about 2 feet can be accomplished by air injection through well points. In one case, air was injected into a series of 10 wells using diffusers attached to paint sprayer-type compressors. They delivered about 2.5 cfm to enhance microbial degradation. Various nutrients were added simultaneously. The diffusers were positioned 5 feet from the bottom of the well and below the water table (Raymond et al. 1976). Aeration through well points has been primarily used for saturated soils and has been shown to be effective. Applicability of the technique for unsaturated soils is not certain.

Table A-1. Soil Modification Requirements For Treatment Technologies*

Technology	Oxygen content	Moisture content	Nutrient content	pH	Temperature
Soil flushing	-	-	-	x	x
Solidification/stabilization					
Pozzolan-portland cement	-	x	-	x	-
Lime-fly ash	-	x	-	x	-
Thermoplastic microencapsulation	-	x	-	-	-
Sorption	-	x	-	x	-
Vitrification	-	x	-	-	-
Degradation					
Chemical degradation					
Oxidation					
Soil-catalyzed reactions	x	-	-	x	-
Oxidizing agents	x	-	-	x	-
Reduction					
Reducing agents	x	x	-	x	-
Chromium	x	-	-	x	-
Selenium	x	-	-	x	-
Dechlorination	-	x	-	-	x
Polymerization	-	-	-	-	-
Biodegradation					
Colloidal gas aphrons		x			
Soil moisture	-	x	-	-	-
Soil oxygen-aerobic	x	-	-	-	-
Soil oxygen-anaerobic	x	x	-	-	-
Soil pH	-	-	x	-	
Nutrients	-	-	x	-	-
Temperature	-	x	-	-	x
Nonspecific org amendments	-	-	-	-	x
Cometabolism					
Analogue enrichment	-	-	x	-	x
Nonanalogue enrichment with methane	x	-	x	-	x
Other nonanalogue hydrocarbon enrichment	-	-	x	-	x
Exogenous acclimated or mutant microorganism	-	-	x	-	x
Cell-free enzymes	-	-	-	-	x
Photolysis					
Proton donors	-	-	-	-	-
Enhanced volatilization	-	x	-	-	-
Control of volatile materials					
Soil vapor extraction	-	x	-	-	-
Radio frequency heating	-	x	-	-	-
Soil cooling	-	x	-	-	x
Chemical and physical separation					
Permeable barriers	-	-	-	x	-
Electrokinetics	-	x	-	x	-
Ground freezing	-	x	-	-	x

Moisture Control

Control of moisture content of soils at an in situ treatment site may be essential for control and optimization of some degradative and sorptive processes, as well as for suppression of volatilization of some hazardous constituents. Moisture control may take the form of supplemental water to the site (irrigation), removal of excess water (drainage, well points), and a combination of techniques for greater moisture control, or other methods, such as soil additives.

Irrigation

Irrigation may be accomplished by subirrigation, surface irrigation, or overhead (sprinkler) irrigation (Fry and Grey 1971).

With subirrigation, water is applied below the ground surface and moves upward by capillary action. If the water has high salinity, salts may accumulate in the surface soil, resulting in an adverse effect on soil microbiological activity. The site must be nearly level and smooth, with either a natural or perched water table, which can be maintained at a desired elevation. The ground water is regulated by check dams and gates in open ditches, or jointed perforated pipe to maintain the water level in soil. The use of such systems is limited by the restrictive site criteria. There may be situations in which a subirrigation system may be combined with a drainage system to optimize soil moisture content. However, at a hazardous waste site, raising the water table might result in undesirable ground-water contamination.

Trickle irrigation is a system of supplying filtered water directly on or below the soil surface through an extensive pipe network with low flow-rate outlets only to areas which require irrigation. It does not give uniform coverage to an area, but with proper management, does reduce percolation and evaporation losses. For most in situ treatment sites, this method would probably not be appropriate, but it may find application in an area where only "hot spots" of wastes are being treated.

Surface irrigation includes flood, furrow, or corrugation irrigation. Since the prevention of off-site migration of hazardous constituents to ground or surface waters is a primary restraint on in situ treatment technology, the use of surface irrigation should be viewed with caution. Contaminated water may also present a hazard to on-site personnel.

In flood irrigation, water covers the surface of a soil in a continuous sheet. Theoretically, water should stay at every point just long enough to apply the desired amount, but this is difficult or impossible to achieve under field conditions.

In corrugation irrigation, as with furrow irrigation, water is applied in small furrows from a head ditch. However, in this case, the furrows are used only to guide the water, and overflooding of the furrows can occur.

In general, control and uniform application of water is difficult with surface irrigation. Also, soils high in clay content tend to seal when water floods the surface, limiting water infiltration.

The basic sprinkler irrigation system consists of a pump to move water from the source to the site, a pipe or pipes leading from the pump to the sprinkler heads, and the spray nozzles. Sprinkler irrigation has many advantages. Erosion and runoff of irrigation water can be controlled or eliminated, application rates can be adjusted for soils of different textures, even within the same area, and water can be distributed more uniformly. Irrigation is also possible on steep, sloping land and irregular terrain. Usually less water is required than with surface flooding methods, and the amount of water applied can be controlled to meet the needs of the in situ treatment technique.

There are several types of sprinkler irrigation systems:

- Permanent installation with buried main and lateral lines.
- Semi-permanent systems with fixed main lines and portable laterals.
- Fully portable systems with portable main lines and laterals, as well as portable pumping plant.

The first two types (especially the first) would likely not be appropriate nor cost-effective for a hazardous waste site because of the required land disturbance for installation and the limited time period for execution of the treatment.

The fully portable systems may have hand-moved or mechanically moved laterals. To eliminate movement by hand, the system may have enough laterals to cover the whole area (a solid set system). Portable systems can be installed in such areas as forests in pattern such as to avoid interference with trees. Mechanically moved laterals may be divided into three categories: side-roll wheel move; center pivot systems; and traveling sprinklers. The amount of labor is considerably reduced compared to portable systems, but the cost of the equipment is higher. The health and safety of workers, however, must be considered as well as cost in the choice of an appropriate system.

The side-roll wheel move is a lateral suspended on a series of wheels. The unit is stationary during operation and is moved while shut off by an engine mounted at the center of the line or an outside power source at one end of the line. A variation of this system is a continuous travel wheel with a flexible hose, which remains in operation as the wheel moves across the field.

The center pivot system is a pipeline suspended above ground with various sized sprinklers spaced along its length. The system is self-propelled and continuously rotates around a pivot point.

The traveling sprinkler consists of a single gun sprinkler mounted on a portable, wheeled unit which is self-propelled up and down the length of the field.

The choice of an appropriate irrigation system depends on site conditions, costs, and health and safety considerations for both on-site personnel and off-site populations. The system should be designed by a qualified specialist such as an agricultural engineer. Preliminary guidelines for designing an irrigation system can be found in the Sprinkler Irrigation Handbook (Fry and Grey 1971) and Planning for an Irrigation System (Turner and Anderson 1980). The latter publication discusses sources of water, including legal rights, and methods of determining irrigation costs, in addition to technical aspects of irrigation.

Drainage

A properly designed drainage system removes excess water and lowers the ground-water level to prevent waterlogging. Surface drainage is accomplished by open ditches and lateral drains, while subsurface drainage is accomplished by a system of open ditches and buried tube drains into which water seeps by gravity. The collected water is conveyed to a suitable disposal point. Subsurface drainage may also be accomplished by pumping from wells to lower the water table. Caution is required at a hazardous waste site to ensure that drainage water disposed off site is not contaminated with hazardous substances. Provision must be made to collect, store, treat, and or recycle water that is not acceptable for offsite release. The drainage system should be managed to prevent or minimize contamination problems.

The design of a drainage system is affected by the topography, soil properties, and water source factors of a site. The two types of drainage systems are (Donnan and Schwab 1974):

- Surface drains - used where subsurface drainage is impractical (e.g., impermeable soils, excavation difficult), to remove surface water or lower water table.
- Subsurface drains - used to lower the water table. Construction materials include clay or concrete tile, corrugated metal pipe, and plastic tubing. Selection depends on strength requirements, chemical compatibility, and cost considerations.

For the design and construction of a drainage system, a drainage engineer should be consulted. The American Society of Agromony monograph, Drainage for Agriculture (Schilfgaarde 1974) contains a complete discussion of drainage.

Well Points

Well points, like subsurface drains, can be used to lower the water table in shallow aquifers. They typically consist of a series of riser pipes screened at the bottom and connected to a common header pipe and centrifugal pump. Well point systems are practical up to 10 meters (33 feet) and are most effective at 4.5 meters (15 feet). Their effectiveness, however, depends on site-specific conditions, such as the horizontal and vertical hydraulic conductivity of the aquifer (Ehrenfeld and Bass 1983).

Additives

Various additives are available to enhance moisture control. For example, the water-retaining capacity of the soil can be enhanced by adding water-storing substances. Three such synthetic substances were recently evaluated by Nimah et al. (1983) for use in arid area soils. They found that available soil water content was increased by two of the products. Water-repelling agents are available which diminish water absorption by soils. On the other hand, water-repelling soils can be treated with surface-active wetting agents to improve water infiltration and percolation. Other soil characteristics which have been modified by surface active agent include acceleration of soil drainage, modification of soil structure, dispersion of clays, and soil made more compactable. Evaporation retardants are also available to retain moisture in a soil. Secondary effects of some of these amendments on soil biological activities, other soil physical properties, soil chemical properties and environmental effects, e.g., leachability and degradability, are discussed by Brandt (1972).

Nutrient Additions To The Soil

Degradation of organic compounds at a hazardous waste site requires an active population of microorganisms. Among other environmental factors (e.g., temperature, moisture, pH, etc.), adequate nutrition is vital to maintain the microbial population at an optimum level. The hazardous wastes being degraded may contribute some necessary nutrients, but may not supply all that are required or that may be beneficial (e.g., silicon and sodium). If the soil does not contain an adequate supply of nutrients, the soil must be supplied with the appropriate elements in the form of fertilizers. A fertilizer is any substance added to the soil to supply those elements required in plant nutrition.

The number of substances suitable as fertilizers is very large, and their compositions and origins differ considerably. Classification systems incorporating many aspects of fertilizer origin, use, and characteristics are presented in Finck (1982). Because of the variety of possible classifications, the choice of an appropriate fertilizer can be complicated, and an agronomist should be consulted to develop a fertilization plan at a hazardous waste site. A plan may include types and amounts of nutrients, timing and frequency of application, and method of application. The nutrient status of the soil and the nutrient content of the wastes must be determined to formulate an appropriate fertilization plan. Basic textbooks on fertilization include *Soil Fertility and Fertilizers* (Tisdale et al. 1985), *Fertilizers and Fertilization* (Finck 1982), and *Fertilizers and Soil Amendments* (Follett et al. 1981).

The development of a fertilization program not only includes the proper selection of fertilizer form and determination of correct fertilizer quantities, but also the selection of an application method. Fertilizers must be transported, stored, and applied so that no chemical or physical changes occur to decrease dispersibility and effectiveness. Improper handling during transportation and storage may result in the creation of safety hazards due to moisture absorption, such as increased flammability, explosiveness, and corrosiveness, or the formation of noxious gases. Improper mixing of fertilizer types before or after application may result in nitrogen losses, immobilization of water-soluble phosphate, or deterioration of distribution properties due to moisture absorption (Finck 1982).

In agricultural application, fertilizers are either applied evenly over an area or concentrated at given points, such as banded along roots. At a hazardous waste site, however, fertilizer will likely be applied evenly over the whole contaminated area and incorporated by tilling, if necessary. Nutrients can also be injected through well points below the plow layer.

With broadcast fertilization, the fertilizer can be left on the surface or incorporated with a harrow (2 to 3 cm deep), a cultivator (4 to 6 cm deep), or a plow (a layer at bottom of furrow, e.g., 15 cm deep). The depth of incorporation depends on the solubility of the fertilizer and the desired point of contact in the soil. In general, nitrate fertilizers move freely, while ammonia nitrogen is adsorbed by soil colloids and moves little until converted to nitrate. Potassium is also adsorbed and moves little except in sandy soils. Phosphorus does not move in most soils. Therefore, potassium and phosphorus need to be applied or incorporated to the desired point of use.

Control of Soil pH

Control of soil pH at an in situ hazardous waste treatment site is a critical factor in several treatment techniques (e.g., metal immobilization, optimum microbial activity). The goal of soil pH adjustment in agricultural application usually is to increase the pH to near neutral values, since natural soils tend to be acidic.

The areas of the country in which the need for increasing soil pH is greatest are the humid regions of the East, South, Middle West, and Far West States. In areas where rainfall is low and leaching is minimal, such as parts of the Great Plain States and the arid, irrigated saline-alkali soils of the Southwest, Intermountain, and Far West States, pH adjustment is usually not necessary. Some soils, especially those high in carbonates, do require the pH to be lowered. However, a hazardous waste-contaminated soil may have substances high in pH, thus necessitating soil acidification.

The most common method of controlling pH is liming. Liming is the addition to the soil of any calcium or calcium- and magnesium-containing compound that is capable of reducing acidity (i.e., raising pH). Lime correctly refers only to calcium oxide, but is commonly used to refer to calcium hydroxide, calcium carbonate, calcium-magnesium carbonate, and calcium silicate slags (Tisdale et al. 1985).

There are several benefits of liming to biological activity. At higher pH values, aluminum and manganese are less soluble. Both of these compounds are toxic to most plants. In addition, phosphates and most micro-elements necessary for plant growth (except molybdenum) are more available at higher pH. Microbial activity is greater at or near neutral pH, which enhances mineralization and degradation processes and nitrogen transformations (e.g., nitrogen fixation and nitrification).

A summary of commonly used liming materials is presented in Table A-2. The choice of liming material depends upon several factors. Calcitic and dolomitic limestones are the most commonly used materials. To be effective quickly, however, these materials must be ground, because the rate of reaction is dependent on the surface in contact with the soil. The finer they are ground, the more rapidly they react with the soil. A more finely ground limestone product, however, usually contains a mixture of fine and coarse particles to effect a pH change rapidly and to still be relatively long-lasting as well as reasonably priced. Many states require that 75 to 100 percent of the limestone pass an 8- to 10-mesh sieve and that 20 to 80 percent pass anywhere from an 8- to 100-mesh sieve (Tisdale et al. 1985). Calcium oxide and calcium hydroxide are manufactured as powders and react quickly.

Other factors to consider in the selection of a limestone are neutralizing value, magnesium content, and cost per ton applied to the land.

Lime requirement for soil pH adjustment is dependent on several factors, including soil texture, type of clay, organic matter content, and exchangeable aluminum (Follett et al. 1981). The buffering capacity of soil reflects the ability of soil components to hold a large number of ions in adsorbed or reserve form. Thus, adsorption or inactivation of H+ ions, or the release of adsorbed ions to neutralize OH- ions provides protection against abrupt changes in pH when acidic or basic constituents are added to the soil. Differences among soils in their buffering capacity reflect differences in the soil cation exchange capacities and will directly affect the amount of lime required to adjust soil pH. The amount of lime required is also a function of the depth of incorporation at the site, i.e., volume of soil to be treated. The amount of lime required to effect a pH change in a particular site/soil/waste system is determined by a state experimental or commercial soil testing laboratory in short-term treatability studies or soil-buffer tests (McLean 1982).

Lime requirements may also be affected by acid precipitation and acid-forming fertilizers. A field study in Connecticut showed that each year the acidity generated by acid precipitation would require 36 kg/ha (32 lb/A) of pure calcium carbonate for neutralization (Frink and Voight 1976).

Table A-2. Liming Materials[*]

Liming material	Description	Calcium carbonate equivalent[†]	Comments
Limestone, calcitic	$CaCO_3$, 100% purity	100	Neutralization value usually between 90-98% because of impurities; pulverized to desired fineness.
Limestone, dolomitic	65% $CaCO_3$ + 20% $MgCO_3$, 87% purity[††]	89	Pure dolomite (50% $MgCO_3$ and 50% $CaCO_3$) has neutralizing value of 109%; pulverized to desired fineness.
Lime, unslaked lime, burned lime, quick lime	CaO, 85% purity	151	Manufactured by roasting calcitic limestone; purity depends on purity of raw materials; white powder, difficult to handle - caustic; quick acting; must be mixed with soil or will harden and cake.
Hydrated lime, staked lime, builder's lime	$Ca(OH)_2$, 85% purity	120	Prepared by hydrating CaO; white powder, caustic, difficult to handle; quickly acting.
Marl	$CaCO_3$, 50% purity	50	Soft, unconsolidated deposits of $CaCO_3$, mixed with earth, and usually quite moist.
Blast furnace slag	$CaSi_2O_3$	75-90	By-product in manufacture of pig iron; usually contains magnesium.
Waste lime products	Extremely variable in composition	—	—

[*] Source: Follett et al. 1981, Tisdale et al. 1985.

[†] Calcium carbonate equivalent (CCE): neutralizing value compared to pure calcium carbonate, which has a neutralizing value defined as 100.

[††] State laws specify a calcium carbonate equivalent averaging 85%.

Lime is usually applied from a V-shaped truck bed with a spinner-type propeller in the back (Follett et al. 1981). Uniform spreading is difficult with this equipment, and wind losses can be significant. A more accurate but slower and more costly method is a lime spreader (a covered hopper or conveyor) pulled by a tractor. Limestone does not migrate easily in the soil since it is only slightly soluble, and must be placed where needed. Plowing and/or discing surface-applied lime into the soil may therefore be required.

The application of fluid lime is becoming more popular, especially when mixed with fluid nitrogen fertilizer. The combination results in less trips across the soil, and the lime is available to counteract acidity produced by the nitrogen. Also, limestone has been applied successfully to a pharmaceutical wastewater land treatment facility through a spray irrigation system.

Modification of Soil Temperature

Soil temperature is one of the more important factors that controls microbiological activity and the rate of organic matter decomposition. Soil temperature is also important in influencing the rate of volatilization of compounds from soil. Soil temperature can be modified by regulating the oncoming and outgoing radiation, or by changing the thermal properties of the soil (Baver et al. 1972).

Vegetation plays a significant role in soil temperature because of the insulating properties of plant cover. Bare soil unprotected from the direct rays from the sun becomes very warm during the hottest part of the day, but also loses its heat rapidly during colder seasons.

However, a well-vegetated soil during the summer does not become as warm as a bare soil, and in the winter, the vegetation acts as an insulator to reduce heat lost from the soil. Frost penetration is more rapid and deeper under bare soils than under a vegetative cover.

Mulches can affect soil temperature in several ways. In general mulches reduce diurnal and seasonal fluctuations in soil temperature. In the middle of the summer, there is little difference between mulched and bare plots, but mulched soil is cooler in spring, winter, and fall, and warms up more slowly in the spring. Mulches with low thermal conductivities decrease heat flow both into and out of the soil; thus, soil will be cooler during the day and warmer during the night. White paper, plastic, or other types of while mulch increase the reflection of incoming radiation, thus reducing excessive heating during the day. A transparent plastic mulch transmits solar energy to the soil and produces a greenhouse effect. A black paper or plastic mulch adsorbs radiant energy during the day and reduces heat loss at night. Humic substances increase soil temperature by their dark color, which increases the soil's heat adsorption.

The type of mulch required determines the application method. Mulches, in addition to modification of soil temperature, are also used to protect soil surfaces from erosion and to reduce water and sediment runoff, prevent surface compaction or crusting, conserve moisture, and help establish plant cover (Soil Conservation Service 1979). A summary of mulch materials is presented in Table A-3. Commercial machines for spraying mulches are available. Hydromulching is a process in which seed, fertilizer, and mulch are applied as a slurry. To apply plastic mulches, equipment which is towed behind a tractor mechanically applies plastic strips which are sealed at the edges with soil. For treatment of large areas, special machines that glue polyethylene strips together are available (Mulder 1979).

Irrigation increases the heat capacity of the soil, raises the humidity of the air, lowers air temperature over the soil, and increases thermal conductivity, resulting in a reduction of daily soil temperature variations (Baver et al. 1972). Sprinkle irrigation, for example, has been used for temperature control, specifically frost protection in winter and cooling in th summer and for reduction of soil erosion by wind (Schwab et al. 1981). Drainage decreases the heat capacity, thus raising the soil temperature. Elimination of excess water in spring causes a more rapid temperature increase. The addition of humic substances improves soil structure, thus improving soil drainability, resulting indirectly in increased soil temperature.

Several physical characteristics of the soil surface can be modified to alter soil temperature (Baver et al. 1972). Compaction of the soil surface increases the density and thus the thermal conductivity. Tillage, on the other hand, creates a surface mulch which reduces heat flow from the surface to the subsurface. The diurnal temperature variation in a cultivated soil is much greater than in an untilled soil. A loosened soil is colder at night and more susceptible to frost.

Table A-3. Mulch Materials*

Organic materials	Quality	Notes
Small grain straw or tame hay	Undamaged, air dry threshed straw, free of undesirable weed seed	Spread uniformly - at least 1/4 of ground should be visible to avoid smothering seedling. Anchor either during application or immediately after placement to avoid loss by wind or water. Straw anchored in place is excellent on permanent seedings.
Corn stalks chopped or shreded	Air dried, shredded into 8" to 12" lengths	Relative slow to decompose. Resistant to wind blowing.
Wood excelsior	Burred wood fibers approximately 4" long	A commercial product packaged in 80-90 lb bales. Apply with power equipment. Tie down usually.
Wood cellulose fiber	Air dry, non-toxic with no growth inhibiting factors	Must be applied with hydraulic seeder.
Compost or manure	Shredded, free of clumps or excessive coarse material	Excellent around shrubs. May create problems with weeds.
Wood chips and bark	Air dried, free from objectionable coarse material	Most effective as mulch around ornamentals, etc. Resistant to wind blowing. May require anchoring with netting to prevent washing or floating off.
Sawdust	Free from objectionable coarse material	More commonly used as a mulch around ornamentals, etc. Requires anchoring on slopes. Tend to crust and shed water.
Pine straw	Air dry. Free of coarse objectionable material	Excellent around plantings. Resistant to wind blowing.
Asphalt emulsion	Slow setting SS-1	Use as a film on soil surface for temporary protection without seeding. Requires special equipment to apply.
Gravel or crushed stone	-	Apply as mulch around woody plants. May be used on seeded areas subject to foot traffic. (Approximate weight - 1 ton per cu. yd).
Wood excelsior mats	Blanket of excelsior fibers with a net backing on one side	Roll 36" x 30 yards covers 161/2 sq. yds. Use without additional mulch. Tie down as specified by manufacturer.
Jute, mesh or net	Woven jute yarn with 3/4" openings	Roll 48" x 75 yds weighs 90 lb. and covers 100 sq. yds.

*Source: Soil Conservation Service 1979.

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Acetaldehyde, 71t, 72t
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Acetone, 20t, 60
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